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Sampling and Analysis of Hazardous Wastes

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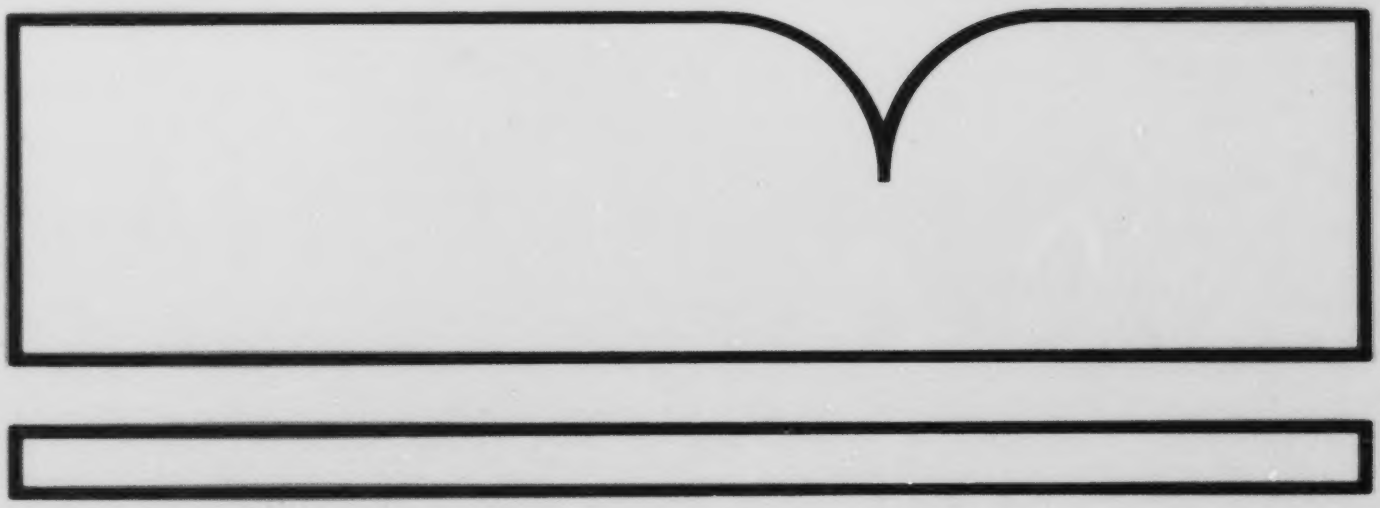

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16. ABSTRACT

This chapter is a relatively brief overview and guide to the very complicated endeavor of sampling and analysis of hazardous waste and related products. Stack sampling and analysis of waste combustion products is emphasized partly due to the authors' backgrounds and partly due to the relatively recent development of most of the technology.

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CHAPTER 8

SAMPLING AND ANALYSIS OF HAZARDOUS WASTES

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8.1 INTRODUCTION

Early attempts to cope with environmental pollution problems generally dealt with one or two specific substances. Flue gas emissions were primarily studied and regulated by the classical SO_x, NO_x, and "particulate" approach. As awareness of potentially harmful effects of more and more materials grew, research studies began to characterize larger numbers of pollutants from a variety of sources. This effort required development of sampling and analysis methods with broader scope and the ability to produce information as cost-effectively as possible (1-3). One of the first regulatory programs to deal with increased numbers of pollutants was the EPA Effluent Guideline Program, for which new sampling and analysis procedures were developed and validated (4-6).

Today, regulators, the regulated community, and researchers alike are still adjusting their approaches and procedures for dealing with hazardous waste problems, caused by hundreds of different compounds in solid, liquid, gaseous, or mixed media. Major programs to develop and validate sampling and analysis methods have been started and are still under way. Many of the

methods are still state-of-the-art technology, and their application requires considerable expertise. The sampling programs and the subsequent analysis efforts are often complex, difficult, and expensive. Success depends on careful planning and execution, as well as thorough knowledge of the field. This chapter is a relatively brief overview and guide to the very complicated endeavor of sampling and analysis of hazardous waste and related products. The references have been selected because of their general usefulness and because they can guide the interested reader to more detailed literature.

8.2 SAMPLING OF HAZARDOUS WASTE AND RELATED PRODUCTS

Sampling of hazardous waste includes a number of diverse activities. It may be necessary to sample waste contained in tanks or drums, in ponds, in piles, or from various processing or transporting equipment such as conveyor belts. In addition, it may be necessary to sample waste that has been diluted or transformed by leaching, spills, or various forms of treatment technology.

Two of the major tasks related to sampling of wastes in any form are planning the sampling strategy and selecting the detailed tactics necessary for support of the strategy. The sampling

strategy must be consistent with the goals of the overall project, and must include selection of major waste impoundments, containers, or streams to be characterized. In addition, the proper degree of sampling resolution must be determined. For example, one might choose to characterize liquid in a waste storage tank, flue gas from an incinerator stack, and water in a scrubber effluent holding pond. One must then decide whether an average value is sufficient for each component of interest in each of these wastes, or whether more detail is needed. Detailed characterization of the materials within each of these units might include the homogeneity of their distribution or the spatial variation of distribution within the unit.

Once the sampling strategy has been developed, detailed tactics can be planned. This planning of tactics includes decisions concerning the number of replicate samples to be taken, whether to combine samples into composites or analyze separately, selection of sampling methods or hardware, selection of sample, packing and shipping methods, and many other seemingly innocuous details. In truth, each of these details may be critical to the

success of the program goal and must be given careful thought and consideration.

8.2.1 Sampling Hazardous Waste

The few basic references in this field invariably point out that hazardous wastes may be complex, multiphase mixtures that have a great variety of physical and chemical properties. As mentioned earlier, the waste itself may be contained in a wide variety of vessels or in ponds or spread throughout sizeable areas of soil. Because of all these possibilities, one standard protocol for sampling hazardous waste cannot be formulated. Each project will require considerable planning and tailoring of the sampling approach to meet the overall objectives.

The strategies and tactics of planning and carrying out the sampling are a great deal more complex than the equipment with which the samples are usually taken. The equipment itself is usually exceptionally simple and inexpensive, especially when compared with the stack-sampling hardware discussed in Section 8.2.2.

Sampling Waste Combustion Products

The methods of selecting the sampling grid, the number of replicates needed, and the expected results in terms of precision and accuracy draw heavily on statistics and cannot be discussed fully in this general overview. The traditional sampling procedures include: simple random, stratified random, systematic random, authoritative, and composite. In simple random sampling, all locations in the batch of waste are identified, and a suitable number of these are randomly selected for sampling. Stratified random sampling is used when the waste is known to be randomly heterogeneous; in this case, the population of locations is stratified to isolate the source of nonrandom distribution, and each stratum may be sampled by simple random sampling. In systematic random sampling, the first unit is sampled randomly, and all other units are selected at fixed intervals from the first: these intervals may be spatial or time intervals. In authoritative sampling, based on an individual's thorough knowledge of the waste, samples are selected according to the known distribution of chemical impurities and are tailored to be consistent with the overall sampling strategy; this procedure is very seldom recommended for hazardous waste, and almost never in a regulatory situation.

When little is known about the distribution of chemical pollutants in the waste, simple random sampling is usually the best choice (7). As one gains more information about the distribution, it may become possible to employ stratified random sampling, systematic random sampling. or even authoritative sampling. For certain applications such as plume definition, geostatistical sampling appears to be a very promising technique (8). The waste sampling references (7-11) contain more detailed discussion of the procedures involved.

Table 8.1 provides examples of sampling equipment commonly used in sampling waste in various containers or impoundments. The following illustration and short descriptions of waste sampling equipment (transferred from reference 7) demonstrate the nature and uses of some of the more common hardware employed.

Composite Liquid Waste Sampler

The composite liquid waste sampler, or Coliwasa (Figure 8.1), is a device employed to sample free-flowing liquids and slurries contained in drums, shallow tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases. The Coliwasa consists of a

glass, plastic, or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled.

Weighted Bottle

The sampler consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise, and open the bottle (Figure 8.2). The weighted bottle samples liquids and free-flowing slurries. A weighted bottle with line is built to the specifications in ASTM Methods D270 and E300.

Dipper

The dipper (Figure 8.3) consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper samples liquids and free-flowing slurries. Dippers are not available commercially and must be fabricated.

Thief

A thief (Figure 8.4) consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and

close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than one-third the width of the slots. A thief is available at laboratory supply stores.

Trier

A trier (Figure 8.5) consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and to loosen soil. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available at laboratory supply stores. A large trier can be fabricated.

Auger

An auger consists of sharpened spiral blades attached to a hard-metal central shaft. An auger samples hard or packed solid wastes or soil. Augers are available at hardware and laboratory supply stores.

Scoops and Shovels

Scoops and shovels are used to sample granular or powdered material in bins, shallow containers, and conveyor belts.

Scoops are available at laboratory supply houses. Flat-nosed shovels are available at hardware stores.

Bailer

The bailer is employed for sampling well water. It consists of a container attached to a cable that is lowered into the well to retrieve a sample. Bailers can be of various designs. The simplest is a weighted bottle or basally capped length of pipe that fills from the top as it is lowered into the well. Some bailers have a check valve, located at the base, which allows water to enter from the bottom as the device is lowered into the well. When the bailer is lifted, the check valve closes, allowing water in the bailer to be brought to the surface. More sophisticated bailers are available that remain open at both ends while being lowered, but can be sealed at both top and bottom by activating a triggering mechanism from the surface. This allows more reliable sampling at discrete depths within a well. Perhaps the best-known bailer of this latter design is the Kemmerer sampler.

Bailers generally provide an excellent means for collecting samples from monitored wells. They can be constructed from a

wide variety of materials compatible with the parameter of interest. Because they are relatively inexpensive, bailers can be easily dedicated to an individual well to minimize cross-contamination during sampling. If not dedicated to a well, they can be easily cleaned to prevent cross-contamination. Unfortunately, bailers are frequently not suited for well evacuation because of their small volume.

Suction Pumps

As the name implies, suction pumps operate by creating a partial vacuum in a sampling tube. This vacuum allows the pressure exerted by the atmosphere on the water in the well to force water up the tube to the surface. Accordingly, these pumps are located at the surface and require only that a transmission tube be lowered into the well. Unfortunately, their use is limited by their reliance on suction to depths of 20 to 25 ft, depending on the pump. In addition, their use may result in outgassing of dissolved gases or volatile organics and is therefore limited in many sampling applications. In spite of this, suction methods may provide a suitable means for well evacuation because the water remaining in the well is left reasonably undisturbed.

Positive Displacement Pumps

A variety of positive displacement pumps is available for use in withdrawing water from wells. These methods use a pumping mechanism placed in the well that forces water from the bottom of the well to the surface by some means of positive displacement. This minimizes the potential for aerating or stripping volatile organics from the sample during removal from the well.

Further details are available about pumps (7) as well as about vacuum extractors, pressure-vacuum lysimeters, and trench lysimeters. The latter three types of devices may be useful for sampling surface water and groundwater.

DeWee, et al. (11), indicate that brushes and vacuum cleaners are useful when sampling dust from hard surfaces.

It is not particularly desirable, and probably not even possible, to list all possible tools or devices that may be used for sampling hazardous waste. As stated earlier, the various hazardous wastes may exhibit a great diversity of properties and may be contained in a wide variety of vessels or impoundments. Performing the sampling properly may call for ingenuity as well as knowledge.

8.2.2 Sampling Waste Combustion Products

The increasing importance of combustion as a disposal technique for hazardous waste has resulted in considerable interest in methods for sampling flue gas emissions. Waste may also be destroyed by cofiring it in industrial boilers or other units such as lime kilns.

Sampling equipment for flue gases is usually more complicated than that used for waste itself, or even for soil and groundwater. This is because the flue gas consists of a multiphase system and is usually at an elevated temperature. Because any of the phases may contain emissions of interest, and many of the combustion products interfere with collection of others, the flue gas must be subjected to filtration, cooling, and various forms of solvent scrubbing or sorption to solid substrates. Measuring gas volumes sampled is thus inherently more difficult and cumbersome than measuring liquid or solid sample volumes or weights.

Of the many sampling devices used over the years, only a few are discussed here. These pieces of equipment are widely used, versatile, and commercially available, and their performances are reasonably well known for the more common pollutants. Readers

interested in more specialized or more exotic sampling approaches can easily locate them in the literature with the aid of the general references given at the end of this chapter.

To ensure that a representative sample is obtained, the sampling probe is usually moved from place to place in the stack according to a prearranged plan. EPA Method 1 (12) gives details on designing the sampling pattern. This practice is called traversing the stack and compensates for stratification of material in the stack.

Another important concept is that of isokinetic sampling. If the velocity of the sample gas drawn into the probe is closely matched to that passing past the probe, the sampling is said to be isokinetic. A mismatch in these velocities results in anisokinetic sampling. Inertial effects during anisokinetic sampling may result in overcollection or undercollection of particulate matter, depending upon its size and mass. This effect does not occur for gases and is generally of marginal importance for particulate material less than 2 μm in diameter

The Source Assessment Sampling System (SASS), Figure 8.6, was developed for environmental assessment programs and is still the

train of choice when large amounts of samples are necessary for extended chemical analysis or biotesting. The SASS includes cyclones for particle sizing, a glass or quartz fiber filter for fine particle collection, a sorbent module for collection of semivolatile organics, and impingers for collection of volatile metals. The SASS operates at 110 to 140 L/min (4 to 5 ft^3/min) and is usually operated long enough to collect 30 m^3 of flue gas.

The large size of the SASS makes traversing inconvenient but not impossible unless precluded by physical arrangements at the sampling site. The particle-sizing cyclones require consistent gas flow (monitored with a pitot tube and manometer) through them for proper operation, which limits flow adjustments necessary for true isokinetic sampling. The SASS has been operated, without the cyclones, in the full traverse and isokinetic sampling mode, but the difficulty of this option makes it unattractive. It is usually operated at a single point in the stack under pseudo-isokinetic conditions. Under most circumstances, this mode of operation results in samples that are indistinguishable from those taken under true isokinetic conditions. Because results may be

less quantitative or representative samples taken in this manner are somewhat less defensible. Further details on this subject are available (13, 14).

Potential corrosion of stainless steel in the sorbent module of the SASS has prompted development of glass sorbent modules, which appear to perform adequately. The glass sorbent module, as well as detailed information concerning construction and operation of both the SASS and the Modified Method Five (MM5) trains is described elsewhere (7, 15).

The MM5 train or semi-VOST (volatile organic sampling train), is conceptually very similar to the SASS but operates at a lower flow rate, usually 14 to 28 L/min (0.5 to 1 ft^3/min). The MM5, shown in Figure 8.7, does not include particle-sizing cyclones and is usually constructed of glass rather than stainless steel. The MM5 results from a very simple modification of any of the commercial sampling trains available that conform to the requirements of EPA Method 5. The sorbent module with cooling capability is simply inserted between the filter and the first impinger. The sorbent module must be positioned vertically so the gas and any condensed liquids flow downward through it.

The sorbent of choice for most sampling jobs for both the SASS and MM5 is XAD-2. Johnson (14) presents a discussion of the reasons behind this choice, as well as of sorbent module placement in the train.

Because of its more convenient size, glass construction, and ready availability, the MM5 is usually chosen over the SASS for incinerator sampling unless larger samples are needed for lower detection limits or extensive analysis requirements.

Either the SASS or MM5 provides collection ability for particulate material, acid gases such as HCl, gaseous metal compounds (if appropriate collection liquids are chosen), medium-boiling organic compounds (b.p. greater than 100 to 300°C), and high-boiling organic compounds (b.p. greater than 300°C). Organic compounds with boiling points between 100 and 120°C require individual attention during the sampling planning stage and may require decreased sampling times to prevent volumetric breakthrough. Volumetric breakthrough is related to the migration rate of sorbed material through unsaturated sorbent beds. This important concept has been discussed further (14).

Considerable field experience has been gained with the SASS and MM5 trains. In recent years, much of the confidence in these trains' ability to collect organic substances rested on knowledge of the behavior of sorbents with respect to collection and recovery. Schlickenrieder et al. (15), discuss this point in more detail. Recent validation studies for selected compounds show excellent collection and recovery and reinforce the general conclusion that the trains are effective (16-18). The MM5 and SASS are not generally quantitative collection trains for organic compounds with boiling points lower than 100°C. For these low-boiling compounds, the recommended methods are plastic sampling bags, glass sampling bulbs, or the newly developed VOST. Because the ambient air at incinerator sites may exhibit relatively high levels of volatile organic compounds, the difficulty is greatly increased in obtaining an uncontaminated sample of low-concentration volatile compounds from the stack. All sampling methods for low levels of volatile compounds are subject to potential contamination and require application with a great deal of care, as well as adequate blanks. All of the above methods have shortcomings, but they are much less severe than the shortcomings and limitations of alternate approaches (12).

The VOST is shown in Figure 8.8. This train and the analysis approach applied to the samples resulting from its use were developed to address stack corcentrations as low as 0.1 ng/L. A sorbent tube containing 1.6 g of Tenax is positioned early in the train to remove organic compounds from the gas and liquid stream as soon as possible. A second sorbent tube containing 1 g of Tenax and 1 g of charcoal follows the condensate collector as a backup in case of breakthrough. The charcoal provides added stopping power for compounds with very low boiling points such as vinyl chloride. The train was designed to use five pairs of sorbent tubes sequentially (plus one pair for range finding), each operating for 20 min at 1 L/min. The ability to concentrate the organics from all five sets of tubes onto one analytical tube and subsequently heat-desorb into a GC or GC/MS makes is possible to detect very low levels of compounds relative to their stack gas concentration. For higher stack gas concentrations, the VOST can and sometimes must be operated at lower flow rates and longer sampling times (limits 0.251 pm for 8 min). This piece of equipment should be useful in a number of operation modes, as long as excessive volumes of gas are not pulled through a single tube, because compounds with low boiling points break through the sorbent after relatively low volumes.

The development and use of the VOST has been discussed in several publications (7, 14, 19-21). References 7 and 20 are particularly helpful to users of this train. Preliminary evidence that the train is effective is given in these references, and an EPA validation project further supports that position (22, 23).

Various types of plastic sampling bags have been used with mixed results. This approach can yield good results, but the sampling and storage characteristics of the specific compound, relative to the specific types of bags to be used, must be well known. For example, organic compounds such as alcohols usually exhibit poor storage characteristics in bags (24). Also, field blanks must be included in the sampling strategy, because all known methods for storing and shipping volatile organic compounds collected from incinerators could allow potentially severe contamination of samples in the field and during transit.

When relatively high concentrations of volatile compounds are sampled, glass sampling bulbs with secure seals may be the best sampling method. Although somewhat inconvenient and lacking in sample-concentrating ability, the glass bulbs do show better sample storage characteristics than plastic bags (24). Because samples cannot be integrated easily with glass bulks, they may not be appropriate for regulatory purposes unless samples are taken in great numbers.

In addition to the methods discussed, special procedures may be necessary for certain pollutants. Formaldehyde is an example of a compound that requires special handling (25). Harris et al. (10) give guidance for such cases. A number of other general sampling approaches exist (13), but are less satisfactory and have not been recommended.

Sampling methods have been discussed that are generally applicable to incineration and to processes closely related to incineration, such as cofiring of waste in industrial boilers and burning of contaminated heating oil. Although some of the methods are relatively new and all require a great deal of care and attention, excellent results can be produced through their application.

Obtaining a representative sample from the stack, particularly in the case of organic emissions, is a complicated and technically difficult process. The most consistent and well-defined result will be obtained by following detailed, written, validated procedures (e.g., 7). The tendency to modify such procedures or replace them with new ones should generally be resisted.

8.2.3 Sampling Solid and Liquid Effluents from Combustors and Control Devices

The methods and equipment previously discussed for use with waste combustion products will often be applicable (7, 10) to sampling solid and liquid effluents. In addition, liquid samples must sometimes by taken from taps. In certain instances, sampling difficulties may require special operation of the equipment. Bottom ash from combustors is often difficult to collect and particularly difficult to relate to a given charge of waste. Sometimes bottom ash can be obtained from pilot units by shutting down operation and collecting the ash from an entire run. S ilar operations have been carried out to obtain boiler tube soot for an entire batch of cofired waste.

8.2.4 Sample Containers, Shipping and Storage

Every step in the sampling and analysis chain of events is critical and cannot be carried out carelessly without detriment to the final result. Container selection guidance given in the references (7, 10) usually recommends glass containers protected against light and excessive heat. Glass is usually recommended because it is relatively inert and easy to clean thoroughly. In

certain circumstances, plastic containers may be preferable and are recommended. The containers must also have secure seals to prevent both sample loss and contamination.

Sample preservation techniques discussed in the literature (7, 26, 27) are specific to the various methods to be used for analysis. Organic pollutants are generally not treated by additives for preservation purposes but are cooled and protected from light.

Shipping must always be done in compliance with Department of Transportation regulations. In addition, thought must be given to acceptable delays before analysis and potential for degradation of the samples. For example, it is not acceptable to transport samples from a VOST in the same truck compartment with organic solvent cans used for spiking waste or cleanup field operations.

Storage conditions after receipt of the samples from the field are just as important as those during shipping, and they follow many of the same guidelines. Organic compounds are often refrigerated and are always protected from light. Other samples should also be treated with care and not exposed to extreme conditions or high levels of chemical contamination.

8.2.5 Quality Control and Quality Assurance

Although QA/QC procedures and planning are more often associated with analysis, they should also be used during the planning and implementation of the sampling operation. The use of field blanks field spiking procedures, and other aspects of QC have a great deal of influence on field sampling operations. The references (7, 10) have detailed discussions of this important subject. Audit procedures and samples have been developed for some of the sampling methods (28, 29), and their use is highly recommended even when not actually required.

8.2.6 Safety

Safety of the personnel involved is the most important consideration in any sampling activity. The hazardous waste involved may require special clothing or equipment such as respirators. Several of the references have more detailed discussions of this subject (7, 9, 10). Efforts should also be made to ensure that safety procedures are not violated during field sampling, regardless of the delay that might ensue. Perhaps the most essential part of the safety program dealing with hazardous-waste-related sampling is a thorough and effective personnel training program.

This should include general training in procedures, as well as an introduction to possible risks to be encountered. In addition, a specific safety-oriented discussion should be carried out with the field crew before each sampling trip, which should deal with specific wastes and hazards that are likely to be encountered at a particular site.

8.3 ANALYSIS OF HAZARDOUS WASTE AND RELATED PRODUCTS

8.3.1 Background

Before any generalizations are made about the analysis of hazardous waste, some explanation as to the magnitude and complexity of the overall problem seems warranted. We must consider such diverse factors as the number of wastes generated, the physical states of the wastes, handling and treatment of the wastes, number of potential compounds, toxic or otherwise, and the routes of entry into the environment. According to EPA estimates, more than 200,000 generators produce over 264 million metric tons of hazardous toxic waste annually in the United States. This waste, if improperly managed, poses a serious threat to human health and the environment. More than 60,000 chemicals are now in use, and untold others are being registered each day (30).

Furthermore, literally thousands of unregistered trace chemicals are associated with the registered chemicals in use. Fortunately, most of these chemicals are not considered harmful and many enhance the quality of life. Of those that are considered hazardous substances, many are considered essential in the manufacturing processes leading to useful products, and others are simply the by-products of a specific process. On the other hand, a significant number of registered hazardous substances are no longer in commercial use.

A wide range of technologies exists that can concentrate, destroy, or immobilize industrially generated hazardous wastes. The commercially available treatment technologies can be categorized into five major types of treatment; physical, chemical, biological, thermal, and fixation/encapsulation. Treatment processes for hazardous wastes perform the following functions: volume reduction, component separation, detoxification, destruction, storage, and material recovery. Because no single process can perform all these functions, several different processes must usually be linked in series for adequate treatment. Additionally, selection of appropriate treatment methods depends on the nature

of the waste, form or physical state of the waste, the volume of the waste, relative economics of the treatment methods, and government regulations.

Incineration has long been recognized as one of the best demonstrated and commercially available technologies for waste destruction. Industrial, high-temperature processes can also destroy certain hazardous waste. A gradual shift to incineration as a preferred method of hazardous waste treatment has resulted from Federal and State legislation regulating the disposal of hazardous waste. It is estimated that about 280 incineration facilities are currently operational, 40 of which are commercial facilities. Industrial, high-temperature processes can also destroy certain hazardous wastes. Thermal destruction is currently used to dispose of about 2 to 4 percent of the hazardous waste generated each year (31, 32).

Methods of measuring and defining toxic and hazardous emissions in the environment have been developed as a result of the Toxic Substances Control Act (TSCA), the Resource Conservation and Recovery Act (RCRA), and the efforts of EPA and industry. The term "hazardous substance" has a very specific meaning according

to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Section 101 (14) of CERCLA defines a hazardous substance as follows:

1. Any substance designated pursuant to Section 311(b) of the Clean Water Act (CWA)
2. Any hazardous waste having characteristics identified under or listed pursuant to Section 3001 of the Solid Waste Disposal Act, otherwise known as the Resource Conservation and Recovery Act (RCRA)
3. Any toxic pollutant listed under Section 307(a) of the CWA
4. Any hazardous air pollutant listed under Section 112 of the Clean Air Act (CAA)
5. Any imminently hazardous chemical substance or mixture with respect to which the Administrator of EPA has taken action pursuant to Section 7 of the Toxic Substances Control Act (TSCA)
6. Any element, compound, mixture, solution or substance the Administrator determines to be hazardous pursuant to Section 102 of CERCLA

There are currently 717 hazardous substances (HSs) composed of 611 unique chemical compounds and 106 waste streams (33). This total does not include chemicals or mixtures that exhibit characteristics of ignitability, corrosivity, reactivity, or toxicity according to 40 CFR 261.20. The toxic and hazardous category contains many different substances; however, organic compounds are the most complex and difficult to measure. The selection of appropriate analytical methods depends on a number of important considerations. These include the compounds of interest, the type of waste, the source type, instrument selectivity/sensitivity, and the desired level of detection. Consideration of cost, though secondary, as well as the intended use of the data, can be equally important in the selection process. The complex nature of organic compounds dictates the complexity of the analytical methods. Also, organic substances can enter the environment via gaseous, liquid, or solid media. Although each medium may require different sampling techniques (Section 8.2) and sample preparation techniques, the analytical methods for most samples contain many steps that are essentially the same.

This section addresses the considerations that are most important in selecting analytical methods for the analysis and management of hazardous waste. Each step of the various processes, from the testing of a waste to the disposal of the waste, must be monitored to ensure that each process is environmentally sound and protects the environment. The analytical methods applicable to the analysis of different types of hazardous waste are described or summarized in the following sections and tables. A brief description of the techology, a summary of each method, and pertinent references are included.

8.2.3 Analytical Methods

Because organic hazardous waste is complex, no single analytical technique is applicable to all wastes. For most samples, the analyst should employ proven analytical techniques that are selective and sensitive. The most universal methods for trace analysis are gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS), and a combination of the methods. More specifically, these combinations include gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS).

The minimum detectable quantity (MDQ) for GC depends on the detector used and ranges from 10^{-9} to 10^{-13} g per injection (34). Samples must be volatile (at least 20 torr at 300°C) but can be gases, liquids, or solids. High-molecular-weight compounds, some ionic compounds or highly polar compounds, and thermally unstable compounds cannot be analyzed directly by GC. In some cases, derivatization or pyrolysis techniques can extend the useful range of the GC. Gas chromatographs are widely used, because they (1) are not expensive, (2) are easy to operate, and (3) give excellent quantitative results; however, GC can only confirm the identity of a substance by retention time alone. This is a major concern when complex waste samples are analyzed and several components could have the same retention time. The MS in a total ion current (TIC) scanning mode may be used to identify a compound. If the identity of a compound is known. selected-ion monitoring (SIM) can be used for quantitation to extend the MDQ and for confirmation and quantitation. The sensitivity of the MS ranges from 10^{-9} to 10^{-12} g. Samples that can be analyzed by GC can be analyzed by MS. The GC/MS is a universal technique, handling all sample types, and it is specific in that it will

usually confirm the structure (identity) of a compound. GC/MS is preferred for trace organic analysis, and the instrumentation is readily available, but it is moderately expensive and requires an experienced operator. It has been estimated that approximately 20 percent of all organic compounds can be determined by GC/MS (35). Fortunately, of those compounds currently of environmental concern, approximately 80 percent are amenable to GC/MS analyses.

Liquid chromatography is recommended for compounds not amenable to gas chromatography. The application of high-performance liquid chromatography (HPLC) to the analysis of waste samples has increased significantly. HPLC can be used for identifying a wide range of less volatile compounds not amenable to GC. Chemically bonded stationary phases for HPLC have greatly improved the separation of a wide variety of compounds. Samples can be liquid or solid, organic or inorganic, and range in molecular weight from 18 to 6 million (34). Selectivity is dependent upon sample type and the detector used. The UV detector is considered the most universal and can measure 10^{-9} g of most species. Aliphatic hydrocarbons are a notable exception because the UV detector is less sensitive to this class of compounds. This lack of sensitivity for

hydrocarbons can frequently be used to advantage, because most environmental samples contain a higher percentage of such compounds than of the analyte of interest. Other LC detectors are more selective and sensitive. For example, for selected compounds, the fluorescence detector can measure 10^{-12} g, and the electrochemical detector can measure 10^{-10} g. Although not yet widely used in waste analyses, the LC/MS combination separates complex mixtures and extends the selectivity of the MS to a large class of organic compounds not amenable to GC/MS analysis. Table 8.2 summarizes the instrumental techniques and detectors widely used for trace analysis.

Reliable analytical measurements of environmental samples are an essential ingredient for making sound decisions involving many facets of society, which include advancing technology, safeguarding the public health, and improving the quality of the environment. The American Chemical Society's Committee of Environmental Improvement (CEI) charged its subcommittee on Environmental Monitoring and Analysis with the task of developing a set of guidelines to improve the quality of environmental analytical measurements (36). The guidelines aid in the evalua-

tion of analytical measurements and in the intelligent choice of methods that meet the requirements of a specific measurement. Analytical objectives often require the measurement of parts-per-million levels in hazardous waste samples and parts- per-billion and even parts-per-trillion levels in hazardous waste combustion effluent samples. Advances in analytical methodology continue to lower the levels of detection to meet these needs. Many factors are of critical importance at these levels and influence the outcome and reliability of environmental measurements. Good planning is essential to ensure that the results are valid and provide a basis on which a process or regulatory decision can be made. The analyst cannot assume that the person requesting an analysis will also be able to define the objectives of the analysis properly.

A protocol that describes the analytical process in detail should include a description of the quality assurance and quality control requirements, the sampling plan, the analytical methods, calculations, and documentation and report requirements. If analytical data are to be used for a screening program or to adjust an operating parameter, an unvalidated method may be adequate. If on the other hand, a regulatory compliance is

involved, a validated analytical method is usually required. To validate a method, the CEI committee recommended that a minimum of three different concentrations of calibration standards be measured in triplicate. The concentrations of the calibration standards must bracket the concentration of the analyte in the sample. No quantitative data should be reported beyond the range of the calibration of the methodology. Internal standards (reference materials) are frequently used for quantitation. Surrogates are frequently used for spiking to determine recovery efficiency during sample preparation. Internal standards are added prior to analyses. Both types of reference materials are chosen to simulate the analyte of interest.

Selection of a proper analytical method is one of the most important factors influencing the reliability of the resulting data. Measurements should be made with tested and documented procedures. Furthermore, each laboratory and analyst must evaluate the methodology by using typical samples to demonstrate competence in the use of the measurement procedure.

To address the analyses of both hazardous waste and products from the combustion of hazardous waste, some assumptions are necessary. Namely, the methods of collection and sample prepara-

tion are different, but the methods of sample analysis (analytical finish) for the final extracts from the waste samples and combustion sources are similar. Tables 8.3 and 8.4 summarize by method number the methods applicable to the analyses of hazardous waste and hazardous waste combustion products (7, 10).

8.3.3 Considerations Associated with Hazardous Waste Analysis

A common expression in the environmental analytical laboratory is "garbage in, garbage out". The integrity of the analytical data is highly dependent on the sample submitted for instrumental analysis. Although most instrumental "finishes" yield final data that are of known quality when standard solutions are analyzed, many methods of sample handling prior to analysis that are variable and matrix dependent are critical to the accuracy of the resulting data. After a sample has been obtained, the analytical protocol often requires extraction and one or more cleanup treatments before the analytes are measured. Sample preparation may involve physical operations such as sieving, blending, crushing, drying, phase separation and/or chemical operations such as dissolution, extraction, digestion, fractionation, derivatization, pH adjustment, and the addition of preservatives, surrogates,

standards, or other materials. These physical and chemical treatments not only add complexity to the analytical process but are potential sources of contamination, mechanical loss, bias, and variance. Therefore, sample preparation should be planned carefully and documented in sufficient detail to provide a complete record of the sample history. Further, samples taken specifically to test the quality assurance system (i.e., quality assurance samples) should be subjected to these same preparation steps.

The analyst must recognize and be aware of the risks that are associated with each form of pretreatment and take appropriate preventative action for each. This may include reporting, correcting for, or possibly removing interferences from the analytes of interest by modifying the protocol. All changes in the protocol must be documented. In most cases, sample stabilization (either by pH adjustment or by quenching of dissolved chlorine), depending on the compounds present, is not necessary if the samples are to be extracted within 48 h of sampling. However, samples containing phenols and benzidine derivatives require immediate stabilization, and samples containing metals and cyanides must be stabilized upon arrival at the laboratory. Both can be

stabilized by pH adjustment. Samples are generally stored at 4 °C. Purgeable samples should be analyzed within 7 days of collection or as requested in the protocol (7 to 14 days). Extractable organic compounds must be extracted within 7 days and analyzed within 30 days of collection. Metals and cyanides should be analyzed within 30 days.

Ideally, samples of source combustion emissions should be kept at low temperatures and analyzed very rapidly after collection to minimize losses of compounds by vaporization and reaction. Samples should be protected from direct light during and after collection. Most of the literature on source sampling has not provided information on sample preservation. Holding time and preservatives for water pollutants and other analytes have been published in the Federal Register. Details of sample handling containers, preservation, and holding times for hazardous wastes are documented in Chapter IV of the SW 846 document (7).

Many organic samples continue to be reactive after sampling. Therefore, a sample, when fresh, may yield different values for the analyte than the same sample after it has been stored. Because of the complexity of hazardous waste samples and the limited selectivity of many analytical methodologies, inter-

ferences are frequently encountered during analysis. Controls to verify that interferents are not present must be used, and appropriate cleanup procedures should be included to eliminate the interferent.

In the analytical process, the recovery of analytes is influenced by factors such as concentration of the analyte, sample matrix, preservation, and time and temperature of storage. In certain cases, compounds can be lost during extraction. Hexachlorocyclopentadiene has a strong tendency to be absorbed on glass and can be lost during liquid-liquid extraction. The sampling medium can also affect the composition of organic emissions. Artifacts have also been reported when Tenax GC is used as the sorbent in source sampling (37). There is also evidence for the decomposition of polynuclear aromatic hydrocarbons (PAHs) collected on fiberglass filters commonly used in source sampling systems. Teflon or Teflon-coated filters, however, appear to be relatively inert (38). Other problems are often encountered in sample preparation. Sample contamination can occur from improperly cleaned glassware, improper storage and sampling handling, impurities in solvents, and carrier gas contamination; and cross-

contamination can occur from analyzing high- and low-level samples in succession. If a high-level sample is run, a blank should be run to check for carryover. Cross-contamination can also occur when volatile samples are prepared and analyzed in a laboratory or even in the same building where liquid-liquid extractions are performed (9, 39). Any volatile solvent in use in the laboratory is a potential candidate to contaminate volatile samples. Blank samples do not eliminate the problem but do help to identify the problem. Corrective action is frequently required before sample analysis can continue.

Emulsions and foaming may occur during sample preparation and analysis. Emulsions can be broken by stirring, filtration, centrifugation, cooling, or simply allowing them to stand for longer periods of time. Foaming can be reduced by antifoam agents or by specially designed purge vessels or in some instances by adding cleaned, glass-melting-point capillary tubes to the purge vessel. Matrix effects can cause a wide variability in recoveries with organic compounds. Therefore, to be valid, recoveries of a spike standard must be determined in the same matrix as the sample (39).

8.3.4 Analysis of Hazardous Waste

The overall strategy for analyzing hazardous waste includes procedures to determine characteristics of the waste and procedures to determine the composition of the waste. Test procedures, or supporting documentation, is required in each of four major areas.

- waste characteristics
- proximate analyses
- survey analyses
- directed analysis

Details of the procedures and recommendations for conducting these tests are given in the literature (7, 10). An overview of the analytical approach for waste characterization is given in Figure 8.9.

8.3.4.1 Characteristics

Wastes are classified as hazardous if they exhibit any of the following characteristics:

- Toxicity
- Corrosivity
- Reactivity
- Ignitability

The Extraction Procedure (EP) Toxicity Test is currently used to determine if the waste exhibits the characteristic of toxicity. The test involves a leaching procedure used to simulate the aqueous leaching of a toxic chemical when the waste is land disposed. The EP toxicity characteristic sets regulatory levels for eight metals, four pesticides, and two herbicides (National Interim Primary Drinking Water Standards have been established). Any waste that exceeds the EP toxicity thresholds (Table 8.5) is considered hazardous. Details of the EP toxicity procedure are given in Method 1310 in the SW 846 document (7). A proposed new rule would revise the EP toxicity test to include regulatory levels of 38 additional compounds. The new Toxicity Characteristic Leaching Procedure (TCLP) expands the leaching to model the behavior of volatile and semivolatile organics. The complete waste evaluation for TCLP will require two extractions, one for volatile and semivolatile compounds and one for metals. Volatile compounds must be extracted in a zero headspace extractor. Contaminants regulated under the proposed TCLP and regulatory levels are given in Table 8.6.

EPA has proposed using the TCLP for the Land Disposal Restrictions Program under RCRA Subtitle C. The list of Land Disposal Hazardous Constituents is given in Table 8.7. Procedures for the analysis of leachates are described under directed analysis and are based on standard methods established for priority pollutants. Methods for determining ignitability (Methods 1010 and 1020), corrosivity (Method 1110), and reactivity are given in the SW 846 document (7).

8.3.4.2 Directed Analyses

Directed analyses allow quantitative measurement of designated principal organic hazardous constituents (POHCs) in a variety of samples. The POHCs listed in 40 CFR Part 261, Appendix VIII, possess a broad spectrum of physical and chemical properties. Because of the high degree of complexity in the field of organic analysis and the parallel complexity of hazardous waste, the only suitable approach to quantitation and confident identification of specific compounds is by either gas or liquid chromatography. Each GC and LC detection method is based on a different operating principle and responds to different compound classes. When the MS, a highly sophisticated detector, is coupled with the

GC, it identifies and quantifies individual compounds by their mass spectra and retention time. The GC/MS analysis procedure is the method of choice for organic analysis and has been designated for the determination of many of the constituents from the Appendix VIII list. This technique is selective and sensitive, and the use of high-resolution capillary columns improves the separation of complex mixtures. Most Appendix VIII compounds are amenable to GC/MS analysis. Other compounds may require analysis by HPLC, and a few other compounds may require compound-specific or compound-class-specific procedures. The GC/MS and LC analysis of organic constituents is briefly summarized below and discussed in Section 8.3.6. Other compound-specific analytical procedures are not discussed in this chapter, but all compounds in Appendix VIII must be considered in the listing of hazardous waste. Analytical methods using these techniques for hazardous waste have evolved from the experience profile of priority pollutant analysis.

By minimizing the number of analytical procedures and enlisting previous experience with priority pollutant analyses, the number of compounds that can be analyzed by a single method

is maximized. Some of the EPA "600" methods shown in Table 8.8 have been adapted to hazardous waste analysis. Methods 624 and 625 have been extended to the determination of many Appendix VIII compounds (5-7, 40). For example, the recommended method for volatile organic compounds is similar to EPA Method 624, and the method for extractable (semivolatile) organic compounds is similar to EPA Method 625. Table 8.9 lists toxic organic compounds that are designated as priority pollutants, Superfund compounds (CERCLA), and selected Appendix IX compounds. This table illustrates that 115 compounds are common to all lists.

The analysis method for volatile POHCs is identical to the method specified in EPA Method 624 and SW 846 Methods 5030 and 8240. Volatile organic compounds can be determined by these methods after appropriate sample-matrix-dependent pretreatment, in a wide variety of samples including water, leachates, wastewater, hazardous waste, and soils. This method uses a purge and trap (PAT) system with an inert purge gas to remove the volatile substances from the waste and collect them on a sorbent trap. The collected volatile compounds are then thermally desorbed from the sorbent cartridge to the GC column (SP-1000 on Carbopak B) and

analyzed by GC/MS. As with all analytical procedures employing complex matrices, the purge efficiency for each volatile compound of interest must be determined.

The method for analyzing semivolatile extractable compounds is equivalent to EPA Method 625 and SW 846 Methods 8250 and 8270, and its resolution and sensitivity are increased by using an SE-54 bonded, fused-silica capillary column, recommended in Method 8270. These methods are based on the acid/base extraction of the waste with aliquots of a suitable organic solvent, SW 846 Methods 3500 and 3550, and subsequent concentration of the extracts to a suitable volume. The acid and base extracts are usually combined for analysis. Some organic liquid wastes may be prepared for screening analysis by dilution with solvent and direct injection (Method 3580). Microliter volumes of sample extracts are injected onto the fused-silica capillary column by using splitless (or split) injection techniques or on-column injection. The mass spectrometer is usually operated in the electron-impact (EI) mode and the full-scan mode to produce mass spectra for identification. Selected surrogates and internal standards must be added to each sample at the appropriate time as detailed in each procedure.

A generalized HPLC/UV method can be used for some other compounds not amenable to GC/MS analysis and for some compounds such as PAHs amenable to analysis by both procedures. The generalized HPLC methods are based on the use of reversed-phase C_{18} columns. Some compounds are not amenable to the generalized HPLC procedures and require specific HPLC procedures (7, 10). A UV detector is recommended for use with screening methods because the detector can measure a wide range of wavelengths from 190 to 600 nm. For screening a sample, most procedures recommend that the initial wavelengths be set at 254 nm. For specific compounds, other wavelengths offer both increased sensitivity and selectivity. Various procedural options for the HPLC method have been described (7, 10).

8.3.5 Analysis of Hazardous Waste Combustion Products

Effluents from hazardous waste combustion must be analyzed to determine if POHCs selected for a trial burn are destroyed in the incineration process and meet the required destruction and removal efficiency (DRE) of >99.99% established for most compounds. Methods for sampling stack effluents were discussed in Section 8.2.3. Other associated streams such as process scrubber water and solid residues (ash) must be analyzed either to deter-

mine the presence of POHCs or to determine other residual contaminants relating to safe and regulated disposal of the products. The analysis of incinerator effluents involves the same considerations as the analysis of noncombusted hazardous waste. As detailed in Section 8.2.3 the method of sample collection is different; therefore, instead of one composite sample, as is the norm for hazardous waste, there may be several different samples from the effluent of a combustion source and other process and residue samples.

Before combustion effluents are analyzed, the waste feed must be analyzed. Samples of waste must be taken in appropriate zero-headspace bottles (40-mL VOA vials) for volatile analysis. A second composite sample is required for analysis of semivolatile compounds. The VOA samples are analyzed by the purge and trap-GC/MS procedure, and the semivolatiles are extracted and analyzed by GC/MS as described earlier.

The waste feed, particulate matter, probe wash, and ash residues from combustion may be analyzed for metals (Table 8.10), if metals are present in the hazardous wste. Digestion and

analysis procedures are given in SW 846 methods. SW 846 Method 3010 is recommended for acid digestion for flame atomic absorption spectrometry (AAS) or Method 3020 for acid digestion for furnace AAS. The metal-containing constituents and the metals on the Appendix VIII list are analyzed either by AAS or inductively coupled argon plasma (ICAP) emission spectroscopy techniques (7). Table 8.11 summarizes recommended SW 846 methods of AAS. The recommended method for ICAP analysis of multielements is SW 846 Method 6010. The sample digestion techniques depend on the instrumentation employed for the analysis. Mercury is analyzed by a cold vapor technique. The ash may also be analyzed for selected organic compounds, normally for those POHCs that are designated for analysis in the stack effluent.

The ash is prepared for organic analysis by Soxhlet extraction with methylene chloride and concentrated in a Kuderna-Danish apparatus and then analyzed by GC/MS or HPLC methods. The ash extract may also be analyzed or screened for other organic compounds by the same general procedures.

Scrubber water and other process waters are analyzed for the same organic compounds designated in the trial burn. These may

include both volatile compounds and semivolatile organic compounds.

The volatile compounds from stack effluents are collected with a VOST system (8.2.2). The volatile POHCs in the stack gas effluent are collected on several pairs of sorbent tubes. The sorbent tubes are thermally desorbed into the purge vessel of a purge and trap instrument and analyzed as described for hazardous waste by EPA Method 624 (SW 846 Method 8240). The purge vessel is necessary to prevent excess water from the sorbent tubes from entering the GC/MS system. The VOST analytical method is directly applicable to compounds with boiling points from 30 to 100°C but with minor modifications can be extended to some compounds with boiling points above and below this range. Water-soluble compounds may give poor recovery with this method, and extra care should be taken to determine if the data are acceptable for these compounds or, alternately, select a new or modified procedure (4-7, 10, 38).

The semivolatile compounds are collected with a comprehensive sampling train as described in Section 8.2.2. The samples for analysis consist of probe wash, particulate matter, sorbent

trap, and condensate. Each sample must undergo sample preparation including extraction and concentration (SW 846 Methods 3500 and 3550) before analysis. The extracts from the component parts of the sampling system may be combined for analysis by GC/MS by EPA Method 625 (SW 846 Method 8270) or for specific compounds by HPLC. Individual extracts may be analyzed if the collection efficiency of a particular part of the sampling system is being evaluated. Figure 8.10 is an overview of the analysis scheme for stack gas samples from the VOST and the MM5 sampling trains (10).

EPA does not currently regulate the emissions of most toxic thermal reaction products commonly called products of incomplete combustion (PICs). For the EPA program, compounds are considered PICs if they are regulated compounds (Appendix VIII) that are detected in the stack emissions but not present in the waste feed at concentrations >100 ppm. In many cases, a PIC may also be designated as a POHC. The formation of PICs that are monitored as POHC emissions results in anomalously low DREs. Field studies by Trenholm et al. (3) and Castaldine et al. (41) have shown that PICs are emitted from hazardous waste thermal destruction systems. Some experimentally observed PICs are shown in Table 8.12.

Current data suggest that for thermal destruction facilities where high degrees of DRE have been achieved for POHCs, PIC emissions are also low (32). Thus, when a POHC is selected, consideration must be given to the potential for the POHC to also be a PIC. For most PICs, the analytical methodology is similar to that described for POHC analysis. Dioxins and furans are notable exceptions and require specific analytical procedures (10, 42-44).

8.3.6 Use of Surrogates

To simplify the overall analytical approach, it has been suggested that surrogates be used to evaluate the performance of an incinerator. A compound may act as a surrogate for a specific waste feed, or for any waste feed and any incinerator. An ideal surrogate would be nontoxic and easily monitored and more stable than any other compounds in the waste. Proposed surrogates include total unburned hydrocarbons (TUHCs) and carbon monoxide (CO), but these may not correlate with DRE. A listed compound in the waste or a thermally stable compound added to the waste feed may serve as a surrogate. Selection of a single organic compound (or several specific compounds) as a surrogate for evaluation of DRE would greatly simplify monitoring requirements. Gas-phase

thermal stability has been proposed as an alternate to heat of combustion as a ranking scheme for selecting a surrogate compound slightly more stable than any listed compound intended for incineration. Some samples of thermally stable compounds are acetonitrile, hexachlorobenzene, monochlorobenzene, tetrachloroethylene, and trichloroethylene. Halogenated compounds such as CF_4, C_2F_6, C_3F_8, CF_3Cl, $C_2F_3Cl_3$, and SF_6, have also been suggested as possible additive candidates (11, 45, 46).

Emissions of CO and TUHCs may not correlate with DRE but do tend to act as indicators for upset conditions. Selecting a thermally stable component of waste feed, or a thermally stable additive, appears to be scientifically defensible and technically feasible. Protocols for the analysis of a few approved surrogates would be more specific and greatly simplify the assessment of incinerator performance.

8.3.7 Documentation

Analytical measurements should be documented to provide easy access to information to support all claims for the results. Laboratory records should be retained in a permanent file for a

length of time set by the government or other legal requirements. All data must be recorded in laboratory notebooks (bound notebooks preferred) and cross-referenced to raw data such as chromatograms and mass spectra stored in the raw data file.

Environmental management has a strong, documented technical data component. A major problem is the conversion of raw data into information needed for decision making in hazardous waste management. At present the reporting of results remains a paper-intensive, manual system. For example, in 1985 the EPA Contract Laboratory Program consisted of approximately 50 laboratories analyzing samples at a rate of 40,000 per year. Current requirements for the delivery of data on a single sample requires a 2 1/4-in.-thick stack of paper. At this rate, EPA will have a stack of paper containing highly technical data 1 1/2 miles high to examine this year. These data must be converted into useful information to support environmental management. In 1983, the idea for an improved system for handling and processing data was suggested. Data would be transmitted by electronic or magnetic means and machine-read into appropriate integrated computer data bases (47). A good start has been made by EPA in evaluating the

feasibility of electronic data transfer, thus substantially improving the efficiency with which EPA handles data. Data assessment for evaluating hazardous waste cleanup will be faster and more accurate in the near future. This approach may be necessary for day-to-day management of data records from waste management facilities.

8.3.8 Quality Assurance/Quality Control

The quality assurance (QA) component of the analysis of environmental samples is of the highest priority. Data from the analysis of soil, air, drinking water, wastewater, sludge, and hazardous waste must be scientifically valid, defensible, and of known and acceptable accuracy and precision. Thus, the QA program must contain procedures for program management and personnel responsibilities, facilities and equipment, data generation and processing, data quality assessment, and corrective actions. Individual QA programs may vary depending upon the nature of the material to be analyzed and the intended use of the final data. However, certain aspects are common to all situations.

Guidance for developing adequate QA program plans is available (48). The QA program plan stipulates the QA policies, objec

tives, management structure, responsibilities, and procedures for a total QA program for the organization performing analytical services. Included in the program plan is information concerning procedures to ensure the generation of reliable data; processes for collecting, reducing, validating, and storing data; procedures for assessing data quality (accuracy and precision); procedures for performing corrective actions; and the schedule for implementation of the requirements.

The scope of a program plan is usually general. However, a QA project plan gives a more detailed description of how the analytical organization will produce quality data for a specific analysis. Every project that involves environmentally related measurements should have a written and approved QA project plan. Guidance for preparing QA project plans is available (49).

A QA project plan may contain one or more of the following items, if they are appropriate for the specific contract.

- Title page with provision for approval signature
- Table of contents
- Project description
- Project organization and responsibility

- QA objectives for measuring data in terms of precision, accuracy, completeness, representativeness, and comparability
- Sample procedures
- Calibration procedure and frequency
- Analytical procedures
- Data reduction, validation, and reporting
- Internal quality-control checks and frequency
- Performance and system audits and frequency
- Preventive-maintenance procedures and schedules
- Routine procedures for assessing data precision, accuracy, and completeness for specific measurement parameters involved
- Corrective action
- Quality-assurance reports to management

QA project plans are usually prepared in a document-control format consisting of information (i.e., section number, revision number, date of revision, and page number) in the upper right-hand corner of each page of the project plan. All 16 items described previously may be considered and addressed. The level of QA

depends on the project and the end-use of the data that are produced. Specific procedures to assess precision and accuracy on a routine basis during the project are described in each QA project plan (7, 10).

8.3.9 Conclusion

The disposal of wastes will remain regulated with greater emphasis on problem wastes and extremely hazardous wastes as they are identified. There will be fewer landfills, and those that do exist will be tightly controlled. There will be more incineration, more material and resource recovery, and more technological development to destroy and detoxify wastes. Ideally, disposal should be the procedure of last resort. However, proper disposal will be needed even years from now. Many materials have little recycle value, they may be too difficult to degrade, or they contain nonflammable materials difficult to incinerate. Other materials are residues from alternate treatment technologies. Proper burial under RCRA will require attention to properly engineered landfills and will require monitoring to ensure that hazardous waste migrates into soil or water supplies. Thus, the analysis of hazardous waste will continue to be a vital part of

the regulation of hazardous waste. Existing methods are now being validated and extended to handle analysis of a large number of hazardous compounds. Also, new methods are being studies for application to environmental analysis. Although there is a lag time before these methods are available for application to the analysis of hazardous waste, the reader would be well advised to consider the merits of new methods as they have been validated and approved for use.

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Table 8.1 Examples of Sampling Equipment for Particular Waste Types

	Waste location or container								
Waste type	Drum	Sacks and bags	Open-bed truck	Closed-bed truck	Storage tanks or bins	Waste piles	Ponds, lagoons, pits	Conveyor belt	Pipe
Free-flowing liquids and slurries	Coliwasa	N/A	N/A	Coliwasa	Weighted bottle	N/A	Dipper	N/A	Dipper
Sludges	Trier	N/A	Trier	Trierr	Trier	*	*		
Moist powders or granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
Dry powders or granules	Thief	Thief	Thief	Thief	*	Thief	Thief	Shovel	Dipper
Sand or packed powders and granules	Auger	Auger	Auger	Auger	Thief	Thief	*	Dipper	Dipper
Large-grained solids	Large trier	Large trier	Large trier	Large trier	Large trier	Large trier	Large trier	Trier	Dipper

*This type of sampling situation can present significant logistical sampling problems, and sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

SOURCE: This table reproduced from "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods." SW-846 Manual, 3d ed. Document No. 955-001-0000001. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., January 1987.

Table 8.2 Techniques for Trace Organic Analysis

Technique	Detector	Estimated sensitivity, g	Selectivity
GC	Thermal conductivity	10^{-9}	universal
	Flame ionization	10^{-11}	universal
	Electron capture	10^{-13}	selective
	Nitrogen phosphorus (nitrogen mode)	10^{-12}	selective
	Nitrogen phosphorus (phosphorus mode)	10^{-13}	selective
	Flame photometric (sulphur mode)	10^{-9}	selective
	Flame photometric (phosphorus mode)	10^{-11}	selective
	Hall electrolytic conductivity	10^{-11}	selective
	Photoionization	10^{-11}	selective
LC	Ultraviolet/visible	10^{-9}	universal
	Electrochemical	10^{-10}	selective
	Fluorescence	10^{-12}	selective
MS	Total ion current	10^{-9}	universal
	Selected ion monitoring	10^{-12}	selective

NOTE: GC = gas chromatography, LC = liquid chromatography, MS = mass spectrometry.

Table 8.3 Test Methods for Evaluation of Solid Wastes
Physical/Chemical Methods SW 846

Procedure	SW 846 method no.
Waste Evaluation Procedures	
Ignitability	1010:1020
Corrosivity	1110
Electrochemical Corrosion Method	1120
Extraction Procedure Toxicity	1310
Multiple Extraction Procedure	1320
Sample Workup Techniques	
Acid Digestion Procedure for Flame Atomic Absorption Spectroscopy	3010
Acid Digestion procedure for Furnace Atomic Absorption Spectroscopy	3020
Acid Digestion of Oils, Greases or Waxes	3030
Digestion Procedure for Oils, Greases or Waxes	3040
Acid Digestion of Sludges	3050
Alkaline Digestion	3060
Separatory Funnel Liquid-Liquid Extraction	3510
Continuous Liquid-Liquid Extraction	3520
Acid-Base Cleanup Extraction	3530
Soxhlet Extraction	3540
Sonication Extraction	3550
Reverse Phase Cartridge Extraction	3560
Column Cleanup of Petroleum Waste	3570
Protocol for Analysis of Sorbent Cartridge from Volatile Organic Sampling Train	3720
Sample Introduction Techniques	
Headspace	5020
Purge and Trap	5030
Multielemental Inorganic Analytical Methods	
Inductively Coupled Plasma Method	6010
Inorganic Analytical Methods	
Antimony (AA, Direct Aspriation)	7040
(AA, Graphite Furnace)	7041
Arsenic (AA, Furnace)	7060
(AA, Gaseous Hydride)	7061
Barium (AA, Direct Aspiration)	7080
(AA, Furnace)	7081
Beryllium (AA, Direct Aspiration)	7090
(AA, Furnace)	7091
Cadmium (AA, Direct Aspiration)	7130
(AA, Furnace)	7131
Chromium (AA, Direct Aspiration)	
(AA, Furnace)	7191
Hexavalent Chromium: Coprecipitation	7195
Hexavalent Chromium: Colorimetric	7196
Hexavalent Chromium: Chelation-Extraction	7197
Hexavalent Chromium: Differential Pulse Polarography	7198
Copper (AA, Direct Aspiration)	7210
(AA, Furnace)	7211
Iron (AA, Direct Aspiration)	7380
(AA, Furnace)	7381
Manganese (AA, Direct Aspiration)	7460
(AA, Furnace)	7461
Mercury	
Mercury in Liquid Waste (Manual Cold-Vapor Technique)	7470
Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)	7471
Nickel (AA, Direct Aspiration)	7520
(AA, Furnace)	7551
Osmium (AA, Direct Aspiration)	7550
(AA, Furnace)	7551
Selenium (AA, Furnace)	7740
(AA, Gaseous Hydride)	7741
Silver (AA, Direct Aspiration)	7760
(AA, Furnace)	7761
Sodium (AA, Direct Aspiration)	7840
(AA, Furnace)	7841
Vanadium (AA, Direct Aspiration)	7910
(AA, Furnace)	7911
Zinc (AA, Direct Aspiration)	7950
(AA, Furnace)	7951
Organic Analytical Methods	
GC Methods	
Halogenated Volatile Organics	8010
Nonhalogenated Volatile Organics	8015
Aromatic Volatile Organics	8020
Acrolein, Acrylonitrile, Acetonitrile	8030

(continued)

Table 8.3 Test Methods for Evaluation of Solid Wastes
Physical/Chemical Methods SW 846
(continued)

Procedure	SW 846 method no.
Organic Analytical Methods	
GC Methods (continued)	
Phenols	8040
Phthalate Esters	8060
Organochlorine Pesticides and PCBs	8080
Nitroaromatics and Cyclic Ketones	8090
Polynuclear Aromatic Hydrocarbons	8120
Organophosphorus Pesticides	8140
Chlorinated Herbicides	8150
GC/MS Methods	
GC/MS Method for Volatile Organics	8240
GC/MS Method for Semivolatile Organics:	
Packed Column Technique	8250
Capillary Column Technique	8270
HPLC Methods	
Polynuclear Aromatic Hydrocarbons	8310
Miscellaneous Compounds	8320
Thioureas and Other Compounds	8330
Formaldehyde: Basic Medium	8410
Formaldehyde: Acidic Medium	8411
Hierarchical Analytical Protocol for Groundwater	8600
Total Aromatics by Ultraviolet Absorption	8610
Total Nitrogen-Phosphorus Gas Chromatographable Compounds	8620
Derivatization Procedure for Appendix VIII Compounds	8630
Miscellaneous Analytical Methods	
Total and Amenable Cyanide	9010
Method for the Determination of Photodegradable Cyanides	9011
Total Organic Halides (TOX) by Microcoulometric Titration	9020
Total Organic Halides (TOX) by Neutron Activation Analysis	9022
Sulfides	9030
Sulfate (Colorimetric, Automated, Chloranilate)	9035
(Colorimetric, Automated, Methylthymol Blue, AA II)	9036
(Gravimetric)	9037
(Turbidimetric)	9038
pH Measurement	9040
Paper Method	9041
Soil pH	9045
Specific Conductance	9050
Total Organic Carbon	9060
Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)	9065
(Colorimetric, Automated 4-AAP with Distillation)	9066
(Spectrophotometric, MBTH with Distillation)	9067
Oil and Grease, total Recoverable (Gravimetric, Separatory Funnel Extraction	9070
Extraction Method for Sludge Samples	9071
Cation Exchange Capacity (Ammonium Acetate)	9080
(Sodium Acetate)	9081
Compatibility Test for Wastes and Membrane Liners	9090
Saturated Hydraulic Conductivity, Saturated Leachate Conductivity and Intrinsic Permeability Methods	9100
Total Coliform: Multiple Tube Permeation Technique	9131
Membrane Filter Technique	9132
Nitrate	9200
Chloride (Colorimetric, Automated Ferricyanide AA I)	9250
(Colorimetric, Automated Ferricyanide AA II)	9251
(Titrimetric, Mercuric Nitrate)	9252
Grease Alpha and Grease Beta	9310
Alpha-Emitting Radium Isotopes	9313
Radium-228	9320

Table 8.4 Sampling and Analysis Method for Hazardous Waste Combustion

Procedure	Method No.
SAMPLE PREPARATION:	
Representative Aliquots from Field Samples	
--Liquids (Aqueous and Organic)	P001
--Sludges	P002
--Solids	P003
Solvent Extraction of Organic Compounds	
--Aqueous Liquids	P021
--Sludges	P022
--Organic Liquids	P023
--Solids	P024
Drying and Concentrating of Solvent Extracts	P031
Digestion Procedures for Metals	P032
Sample Cleanup Procedures	
--Florisil	P041
--Biobeads SC-3	P042
--Silica Gel	P043
--Alumina	P044
--Liquid/Liquid Extraction	P045
ANALYSIS:	
Ignitability	C001
Corrosivity	C002
Reactivity	C003
Extraction Procedure Toxicity	C004
Moisture, Solid, and Ash Content	A001-A002
Elemental Composition	A003
Total Organic Halogens	A004
Viscosity	A005
Heating Value of the Waste	A006
Survey Analysis of Organic Content	
--Total Chromatographable Organics	A011
--Gravimetric Value	A012
--Volatiles	A013
--Infrared	A014
--Mass Spectrometric	A015
--GC/MS	A016
--HPLC/IR or HPLC	A017

(continued)

Table 8.4 Sampling and Analysis Method for Hazardous Waste Combustion (continued)

Procedure	Method No.
ANALYSIS: (continued)	
Survey Analysis of Inorganics	
Analytical Methods	
--Volatiles	A101
--VOST	A102
--Extractables	A121
--HPLC/UV	A122-A124
--HPLC/Fluorescence	A125
--Aldehydes/Ketones	A131
--Carboxylic Acids	A133
--Oximes	A183
--Organometallics	A191
--Metals	A211-A245
--Anions	A252-A254; A256
--Gases	A141

SOURCE: J.C. Harris, D.J. Larsen, C.E. Rechsteiner, and K.E. Thrun, "Sampling and Analysis Methods for Hazardous Waste Combustion." EPA-600/8-84-002, PB 84-155845, February 1984.

Table 8.5. EPA Toxicity Threshold Levels

Contaminant	Threshold level, mg/L
Herbicides	
2,4-D	10.0
2,4,5-TP	1.0
Metals	
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium (VI)	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Pesticides	
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5

Table 8.6 Toxicity Characteristic Contaminants and Regulatory Levels

Contaminant	Regulatory level, mg/L
Acrylonitrile	5.0
Arsenic	5.0
Barium	100
Benzene	0.07
Bis(2-chloroethyl) ether	0.05
Cadmium	1.0
Carbon disulfide	14.4
Carbon tetrachloride	0.07
Chlordane	0.03
Chlorobenzene	1.4
Chloroform	0.07
Chromium	5.0
o-Cresol	10.0
m-Cresol	10.0
p-Cresol	10.0
2,4-D	1.4
1,2-Dichlorobenzene	4.3
1,4-Dichlorobenzene	10.8
1,2-Dichloroethane	0.40
1,1-Dichloroethylene	0.1
2,4-Dinitrotoluene	0.13
Endrin	0.003
Heptachlor	0.001
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.72
Hexachloroethane	4.3
Isobutanol	36
Lead	5.0
Lindane	0.06
Mercury	0.2
Methoxychlor	1.4
Methylene chloride	8.6
Methyl ethyl ketone	7.2
Nitrobenzene	0.13
Pentachlorophenol	3.6
Phenol	14.4
Pyridine	5.0

(continued)

Table 8.6 Toxicity Characteristic Contaminants and Regulatory Levels (continued)

Contaminant	Regulatory level, mg/L
Selenium	1.0
Silver	5.0
1,1,1,2-Tetrachloroethane	10.0
1,1,2,2-Tetrachloroethane	1.3
Tetrachloroethylene	0.1
2,3,4,6-Tetrachlorophenol	1.5
Toluene	14.4
Toxaphene	0.07
1,1,1-Trichloroethane	30
1,1,2-Trichloroethane	1.2
Trichloroethylene	0.07
2,4,5-Trichlorophenol	5.8
2,4,6-Trichlorophenol	0.30
2,4,5-TP (Silvex)	0.14
Vinyl chloride	0.05

Table 8.7 Land Disposal Constituents

Hazardous constituent	Concentration, mg/L
Acetone	2.0
n-Butyl alcohol	2.0
Carbon disulfide	2.0
Carbon tetrachloride	0.1
Chlorobenzene	2.0
Cresols	2.0
Cyclohexanone	2.0
Ethylene acetate	2.0
Ethylene benzene	2.0
Ethyl ether	2.0
HxCDD-All Hexachlorodibenzo-p-dioxins	0.001
HxCDF-All Hexachlorodibenzofurans	0.001
Isobutanol	2.0
Methanol	2.0
Methylene chloride	1.2
Methyl ethyl ketone	2.0
Methyl isobutyl ketone	2.0
Nitrobenzene	0.09
PeCDD-All Pentachlorodibenzo-p-dioxins	0.001
PeCDF-All Pentachlorodibenzofurans	0.001
Pentachlorophenol	1.0
Pyridine	0.7
TCDD-All Tetrachlorodibenzo-p-dioxins	0.001
TCDF-All Tetrachlorodibenzofurans	0.001
Tetrachloroethylene	0.015
2,3,4,6-Tetrachlorophenol	2.0
Toluene	2.0
1,1,1-Trichloroethane	2.0
1,2,2-Trichloro-1,2,2-trifluoroethane	2.0
Trichloroethylene	0.1
Trichlorofluoromethane	2.0
2,4,5-Trichlorophenol	8.0
2,4,6-Trichlorophenol	0.04
Xylene	2.0

Table 8.8 Methods for Chemical Analyses of Water and Wastes

EPA reference method	Priority pollutants	Method of analysis
601	Purgeable halocarbons	Purge-and-trap (PAT), GC, detection with a Hall (electrolytic) detector
602	Purgeable aromatics	PAT, GC, photoionization detector
603	Acrolein and Acrylonitrile	PAT, GC flame ionization detector
604	Phenols	Extraction, Kuderna-Danish (KD) concentration GC, flame ionization-electron capture detection
605	Benzidines	Extraction, concentration, HPLC, electrochemical detection
606	Phthalate esters	Extraction, Florisil or alumina cleanup KD concentration, GC, flame ionization-capture detection
607	Nitrosamines	Extraction, Florisil or alumina cleanup KD concentration, GC, flame ionization-electron capture detection
608	Organochlorine pesticides and PCBs	Extraction, Florisil or alumina cleanup, KD concentration, GC, detection
609	Nitroaromatics and isophorone	Extraction, KD concentration, GC, flame ionization-electron capture detection

(continued)

Table 8.8 Methods for Chemical Analyses of Water and Wastes (continued)

EPA reference method	Priority pollutants	Method of analysis
610	Polynuclear aromatic hydrocarbons	Extraction, KD concentration, GC, flame ionization detection or HPLC UV fluorescence detection
611	Haloethers	Extraction, solvent exchange, KD concentration, GC, electron capture detection
612	Chlorinated hydrocarbons	Extraction, solvent exchange, KD concentration, GC, electron capture detection
613	2,3,7,8-Tetrachlorodibenzo-p-dioxin	Spiking with labeled 2,3,7,8-TCDD, extraction, solvent exchange, KD concentration, analysis by GC/MS
624	Volatile organic comopunds (purgeable)	PAT analysis by GC/MS
625	Semivolatile Organic compounds (base neutral and acid extractable compounds)	Extraction, KD concentration, analysis by GC/MS

Table 8.9 Listing of Toxic Organics

Common name	Priority Pollutant	Superfund list	Appendix IX	Common name	Priority pollutant	Superfund list	Appendix IX
Organics							
acenaphthene	X	X	X	benzyl alcohol		X	X[a]
acenaphthylene	X	X	X	alpha-BHC	X	X	X
acetone		X	X[a]	beta-BHC	X	X	X
acetonitrile	X		X	delta-BHC	X	X	X
acetophenone			X	gamma-BHC	X	X	X
2-acetylaminofluorene			X	bis(2-chloroethoxy)methane	X	X	X
acrolein	X		X	bis(2-chloroethyl)ether	X	X	X
acrylonitrile	X		X	bis(2-chloroisopropyl)ether	X	X	X
aldrin	X	X	X	bis(2-ethylhexyl)phthalate	X	X	X
allyl alcohol			X	bromodichloromethane	X	X	X
4-aminobiphenyl			X	bromomethane	X	X	X
aniline			X	4-bromophenyl phenyl ether	X	X	X
anthracene	X	X	X	butyl benzyl phthalate	X	X	X
aramite			X	2-sec-butyl-4,6-dinitrophenol			X
Aroclor 1016	X	X	X	carbon disulfide		X	X
Aroclor 1221	X	X	X	carbon tetrachloride	X	X	X
Aroclor 1232	X	X	X	chlordane	X	X	X
Aroclor 1242	X	X	X	p-chloroaniline		X	X
Aroclor 1248	X	X	X	chlorobenzene	X	X	X
Aroclor 1254	X	X	X	chlorobenzilate			X
Aroclor 1260	X	X	X	2-chloro-1,3-butadiene			X
benzene	X	X	X	p-chloro-m-cresol	X		X
benzenethiol			X	chlorodibromomethane	X	X	X
benzidine	X		X	chloroethane	X	X	X
benzo(a)anthracene	X	X	X	2-chloroethyl vinyl ether	X	X	X
benzo(b)fluoranthene	X	X	X	chloroform	X	X	X
benzo(k)fluoranthene	X	X	X	chloromethane	X	X	X
benzoic acid		X	X[a]	2-chloronaphthalene	X	X	X
benzo(a)pyrene	X	X	X	2-chlorophenol	X	X	X
benzo( )pyrene	X	X	X	4-chlorophenyl phenyl ether	X	X	X
p-benzoquinone			X	3-chloropropene			X

(continued)

Table 8.9 Listing of Toxic Organics
(continued)

Common name	Priority Pollutant	Superfund list	Appendix IX	Common name	Priority pollutant	Superfund list	Appendix IX
Organics (continued)							
3-Chloropropionitrile			X	1,2-dichloropropane	X	X	X
chrysene	X	X	X	cis-1,3-dichloropropene	X	X	X
ortho-cresol		X	X	trans-1,3-dichloropropene		X	X
para-cresol		X	X	dieldrin	X	X	X
4,4'-DDD	X	X	X	diethyl phthalate	X	X	X
4,4'-DDE	X	X	X	O,O-diethyl-O,2-pyrazinyl			
4,4'-DDT	X	X	X	phosphorothioate			X
dibenzo(a,h)anthracene	X	X	X	3,3'-dimethoxybenzidine			X
dibenzofuran		X	A	p-dimethylaminoazobenzene			X
dibenzo(a,e)pyrene			X	7,12-dimethylbenz(a)-			
dibenzo(a,h)pyrene			X	anthracene			X
dibenzo(a,i)pyrene			X	3,3'-dimethylbenzidine			X
1,2-dibromo-3-chloro-				alpha, alpha-dimethyl-			
propane			X	phenethylamine			X
1,2-dibromomethane			X	2,4-dimethylphenol	X	X	X
dibromomethane			X	dimethyl phthalate	X	X	X
di-n-butyl phthalate	X	X	X	m-dinitrobenzene			X
m-dichlorobenzene	X	X	X	4,6-dinitro-o-cresol	X	X	X
o-dichlorobenzene	X	X	X	2,4-dinitrophenol	X	X	X
p-dichlorobenzene	X	X	X	2,4-dinitrotoluene	X	X	X
3,3'-dichlorobenzidine	X	X	X	2,6-dinitrotoluene	X	X	X
trans-1,4-dichloro-2-				di-n-octyl phthalate	X	X	X
butene			X	1,4-dioxane			X
dichlorodifluoromethane			X	diphenylamine			X
1,1-dichloroethane	X	X	X	1,2-diphenylhydrazine	X		X
1,2-dichloroethane	X	X	X	di-n-propylnitrosamine	X	X	X
1,1-dichloroethylene	X	X	X	disulfoton			X
trans-1,2-dichloroethylene	X	X	X	endosulfan sulfate	X	X	
dichloromethane	X	X	X	endosulfan I (alpha)	X	X	X
2,4-dichlorophenol	X	X	X	endosulfan II (beta)	X	X	X
2,6-dichlorophenol			X	endrin	X	X	X
2,4-dichlorophenoxy-				endrin aldehyde	X		X
acetic acid			X	endrin ketone		X	

(continued)

Table 8.9 Listing of Toxic Organics
(continued)

Common name	Priority Pollutant	Superfund list	Appendix IX
Organics (continued)			
ethyl benzene	X	X	X[a]
ethyl cyanide			X
ethylene oxide			X
ethyl methacrylate			X
famphur			X
fluoranthene	X	X	X
fluorene	X	X	X
heptachlor	X	X	X
heptachlor epoxide	X	X	X
hexachlorobenzene	X	X	X
hexachlorobutadiene	X	X	X
hexachlorocyclopentadiene	X	X	X
hexachlorodibenzo-p-dioxins			X
hexachlorodibenzofurans			X
hexachloroethane	X	X	X
hexachlorophene			X
hexachloropropene			X
2-hexanone		X	X[a]
indeno(1,2,3-cd)pyrene	X	X	X
iodomethane			X
isobutyl alcohol			X
isodrin			X
isophorone	X	X	A
isosafrole			X
kepone			X
malononitrile			X
methacrylonitrile			X
methapyrilene			X
methoxychlor		X	X
3-methylcholanthrene			X
4,4'-methylene-bis(2-chloroaniline)			X
methyl ethyl ketone		X	X
methyl methylacrylate			X
methyl methanesulfonate			X
2-methylnaphthalene		X	X[a]
methyl parathion			X
4-methyl-2-pentanone		X	X[a]
2-methylphenol		X	
4-methylphenol		X	
naphthalene	X	X	X
1,4-naphthoquinone			X
1-naphthylamine			X
2-naphthylamine			X
m-nitroaniline		X	X[a]
o-nitroanline		X	X[a]
p-nitroaniline		X	X
nitrobenzene	X	X	X
2-nitrophenol	X	X	X[a]
4-nitrophenol	X	X	X
N-nitrosodi-n-butylamine			X
N-nitrosodiethylamine			X
N-nitrosodimethylamine	X		X
N-nitrosodiphenylamine		X	X
N-nitrosomethylethylamine			X
N-nitrosomorpholine			X
N-nitrosopiperidine			X
N-nitrosopyrrolidine			X
5-nitro-o-toluidine			X
parathion			X
pentachlorobenzene			X
pentachlorodibenzo-p-dioxins	X		X
pentachlorodibenzofurans			X
pentachloroethane			X

(continued)

Table 8.9 Listing of Toxic Organics
(continued)

Common name	Priority Pollutant	Superfund list	Appendix IX
Organics (continued)			
pentachloronitrobenzene			X
pentachlorophenol	X	X	X
phenacetine			X
phenanthrene	X	X	X
phenol	X	X	X
phorate			X
2-picoline			X
pronamide			X
2-propyn-1-ol			X
pyrene	X	X	X
pyridine			X
resorcinol			X
safrole			X
silvex			X
styrene		X	X[a]
2,4,5-T			X
1,2,4,5-tetrachlorobenzene			X
2,3,7,8-tetrachlorodibenzo-p-dioxin	X		X
tetrachlorodibenzo-p-dioxins			X
tetrachlorodibenzofurans			X
1,1,1,2-tetrachloroethane			X
1,1,2,2-tetrachloroethane	X	X	X
tetrachloroethylene	X	X	X
2,3,4,6-tetrachlorophenol			X
tetraethyldithiopyro-phosphate			X
toluene	X	X	X
toxaphene	X	X	X
tribromomethane	X	X	X
1,2,4-trichlorobenzene	X	X	X
1,1,1-trichloroethane	X	X	X
1,1,2-trichloroethane	X	X	X
trichloroethylene	X	X	X
trichloromethanethiol			X
trichloromonofluoro-methane			X
2,4,5-trichlorophenol		X	X
2,4,6-trichlorophenol	X	X	X
1,2,3-trichloropropane			X
tris(2,3-dibromopropyl) phosphate			X
vinyl acetate		X	X[a]
vinyl chloride	X	X	X
total xylenes		X	X[a]

[a]Added from Superfund list.

Table 8.10 Toxic Inorganic Substances

Common name	Priority pollutant	Appendix IX[a]	Superfund list
Metals			
aluminum		X[b]	X
antimony	X	X	X
arsenic	X	X	X
barium		X	X
beryllium	X	X	X
cadmium	X	X	X
calcium		X[b]	X
chromium	X	X	X
cobalt		X[b]	X
copper	X	X	X
iron	X	X[b]	X
lead	X	X	X
magnesium		X[b]	X
manganese		X[b]	X
mercury	X	X	X
nickel	X	X	X
osmium		X	
potassium		X[b]	X
selenium	X	X	X
silver	X	X	X
sodium		X[b]	X
thallium	X	X[b]	X
tin		X[b]	X
vanadium		X	X
zinc	X	X	X
Miscellaneous			
cyanide	X	X	X
fluoride		X	
phenols	X		
sulfide		X	

[a]Derived from Appendix VIII.
[b]Added from Superfund List.

Table 8.11 Recommended (AAS) Analysis Methods

Element	SW 846 method no.	Description
Ag	7760	Direct aspiration
	7761	Graphite furnace
As	7060	Graphite furnace
	7061	Gaseous hydride method
Ba	7080	Direct aspiration
	7081	Graphite furnace
Be	7090	Direct aspiration
	7091	Graphite furnace
Cd	7130	Direct aspiration
	7131	Graphite furnace
Cr	7190	Direct aspiration
	7191	Graphite furnace
	7195	Hexavalent Cr: Coprecipitation
	7196	Hexavalent Cr: Colorimetric
	7197	Hexavalent Cr: Chelation-Extraction
	7198	Hexavalent Cr: Differential Pulse Polarography
Cu	7120	Direct aspiration
	7121	Graphite furnace
Hg	7470	Hg in liquid waste (Manual cold vapor technique)
Ni	7520	Direct aspiration
	7521	Graphite furnace
Os	7550	Direct aspiration
	7551	Graphite furnace
Pb	7420	Direct aspiration
	7421	Graphite furnace

(continued)

Table 8.11 Recommended (AAS) Analysis Methods (continued)

Element	SW 846 method no.	Description
Sb	7040	Direct aspiration
	7041	Graphite furnace
Ti	7840	Direct aspiration
	7841	Graphite furnace
V	7910	Direct aspiration
	7911	Graphite furnace
Zn	7950	Direct aspiration
	7951	Graphite furnace

Table 8.12 Experimentally Observed PICs

Parent (POHC)	Product (PIC/POHC)
Chloroform	Tetrachloroethylene Carbon tetrachloride
Carbon tetrachloride	Tetrachloroethylene Hexachloroethane
Toluene	Benzene
Chlorobenzene	Benzene
Trichlorobenzene	Dichlorobenzene Chlorobenzene
Pentachloroethane	Tetrachloroethylene
Polychlorinated biphenyls	Chlorinated dibenzofurans
Polychlorianted phenols	Chlorinated dibenzodioxins
Kepone	Hexachlorobenzene

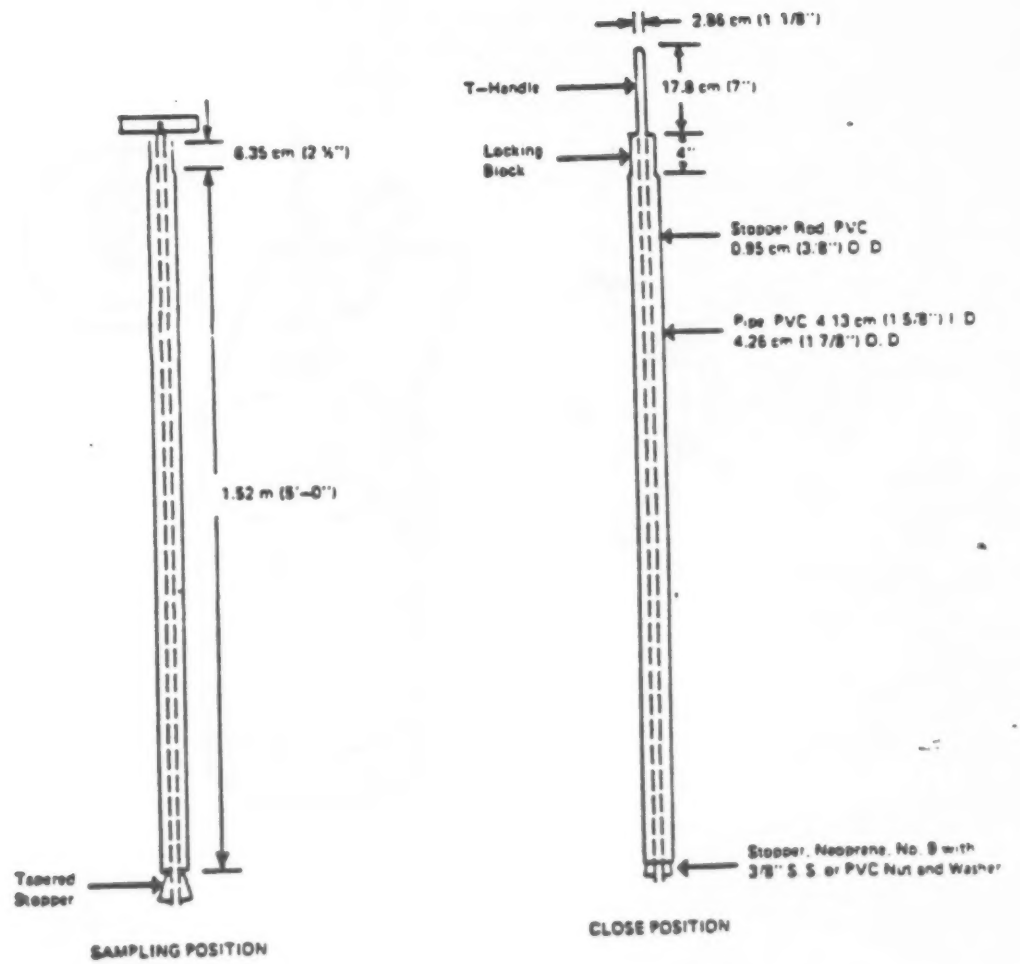


Figure 8-1. Composite liquid waste sampler (Coliwasa).

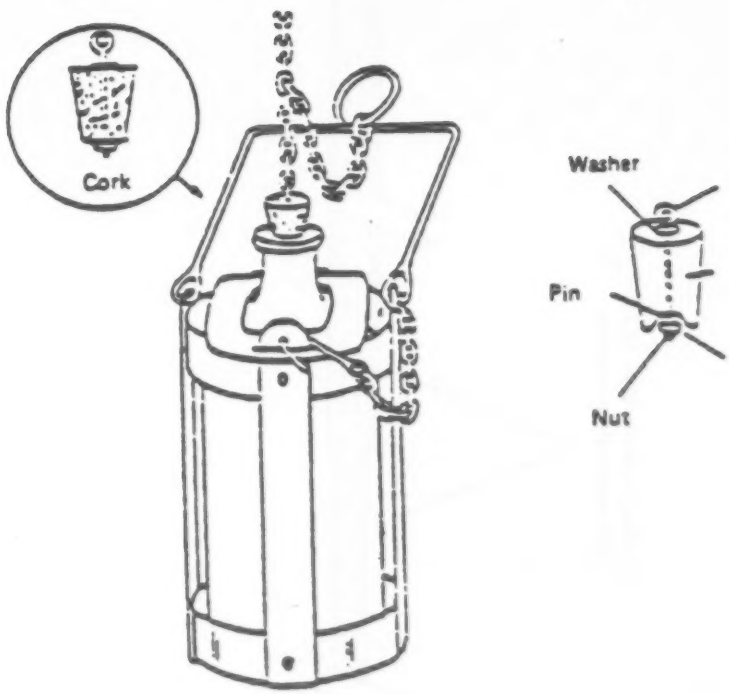


Figure 8-2. Weighted bottle sampler.

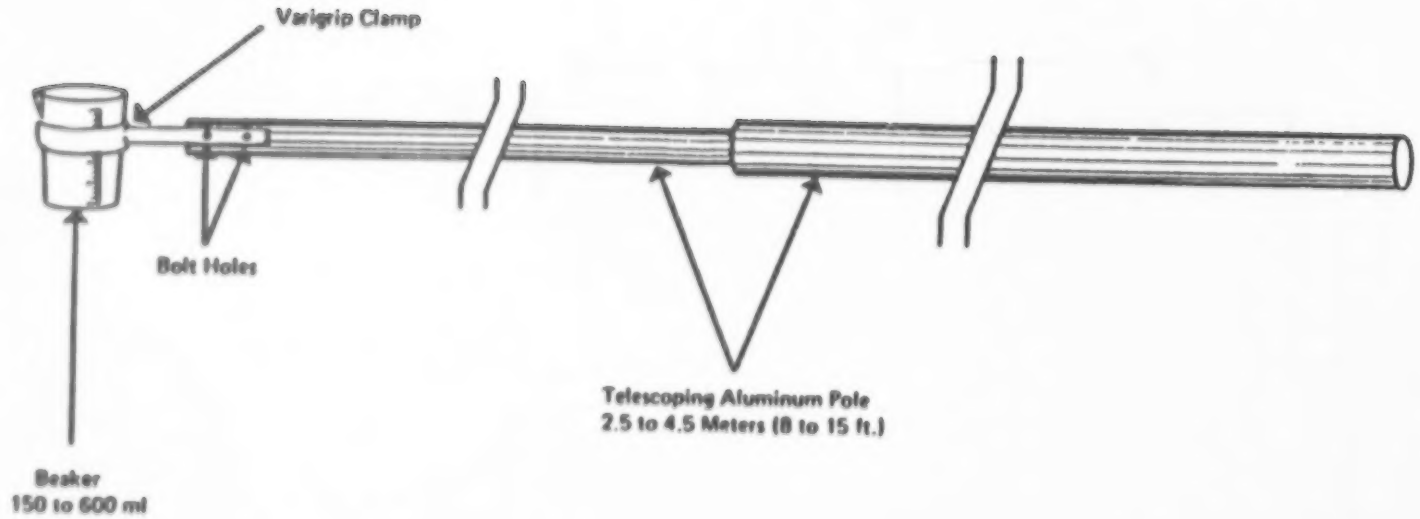


Figure 8-3. Dipper

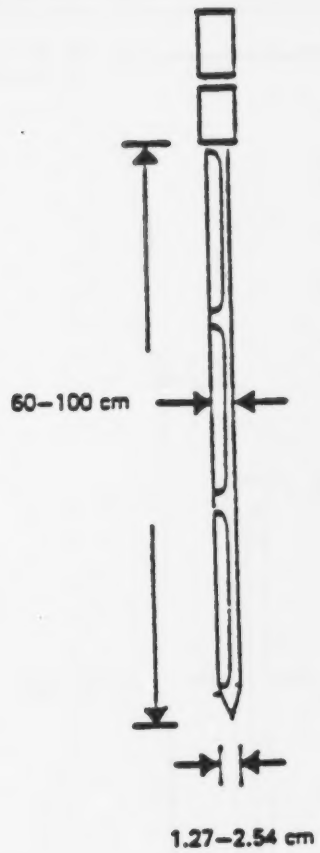
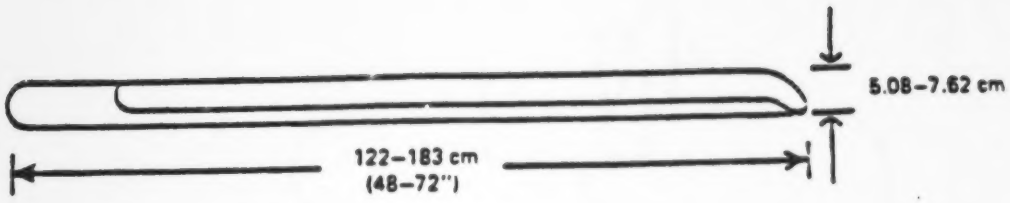


Figure 8-4. Thief sampler.



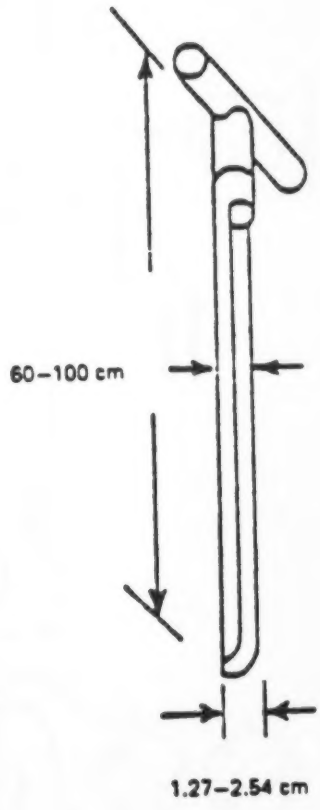


Figure 8-5. Sampling triers.

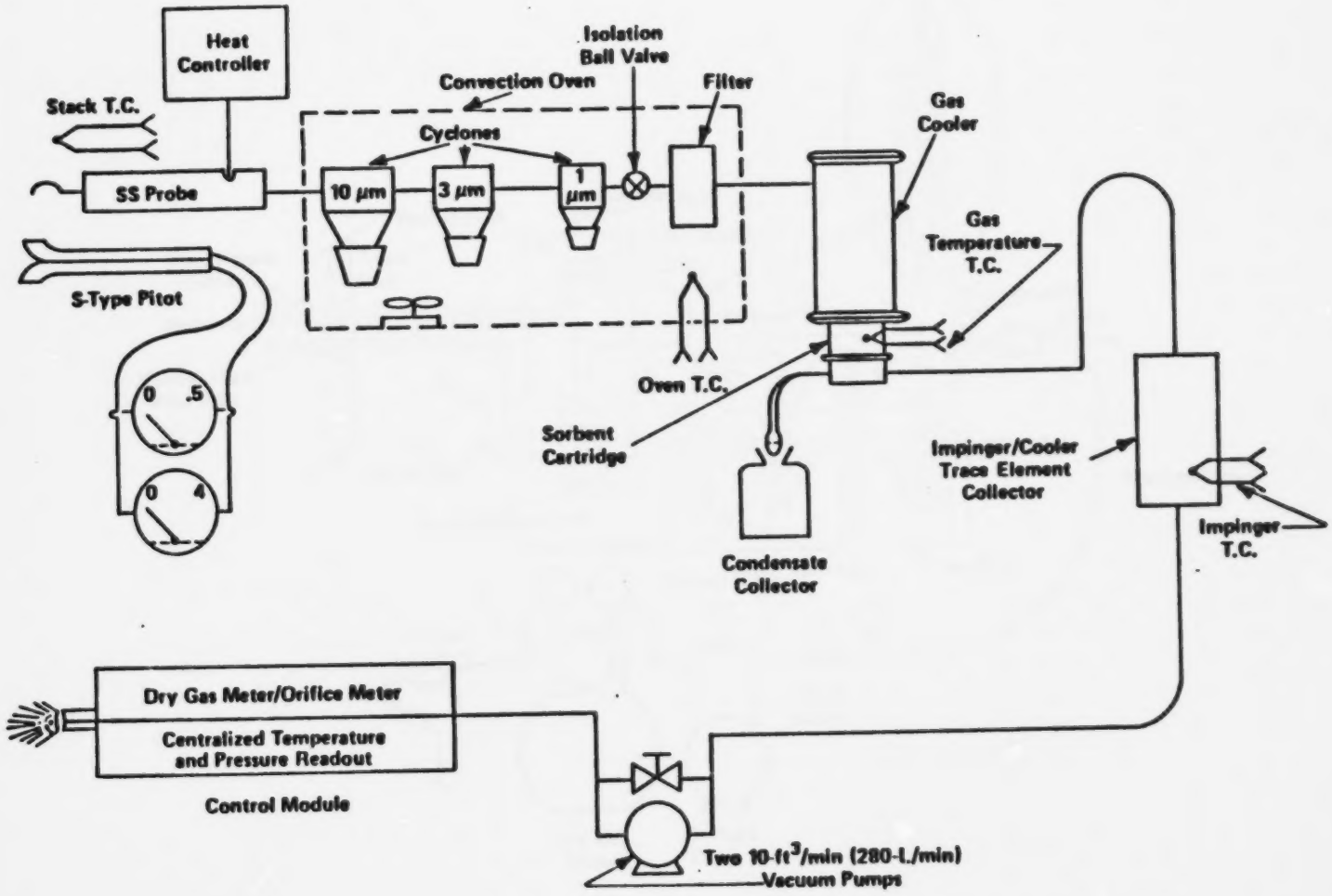


Figure 8-6. Source assessment sampling system (SASS).

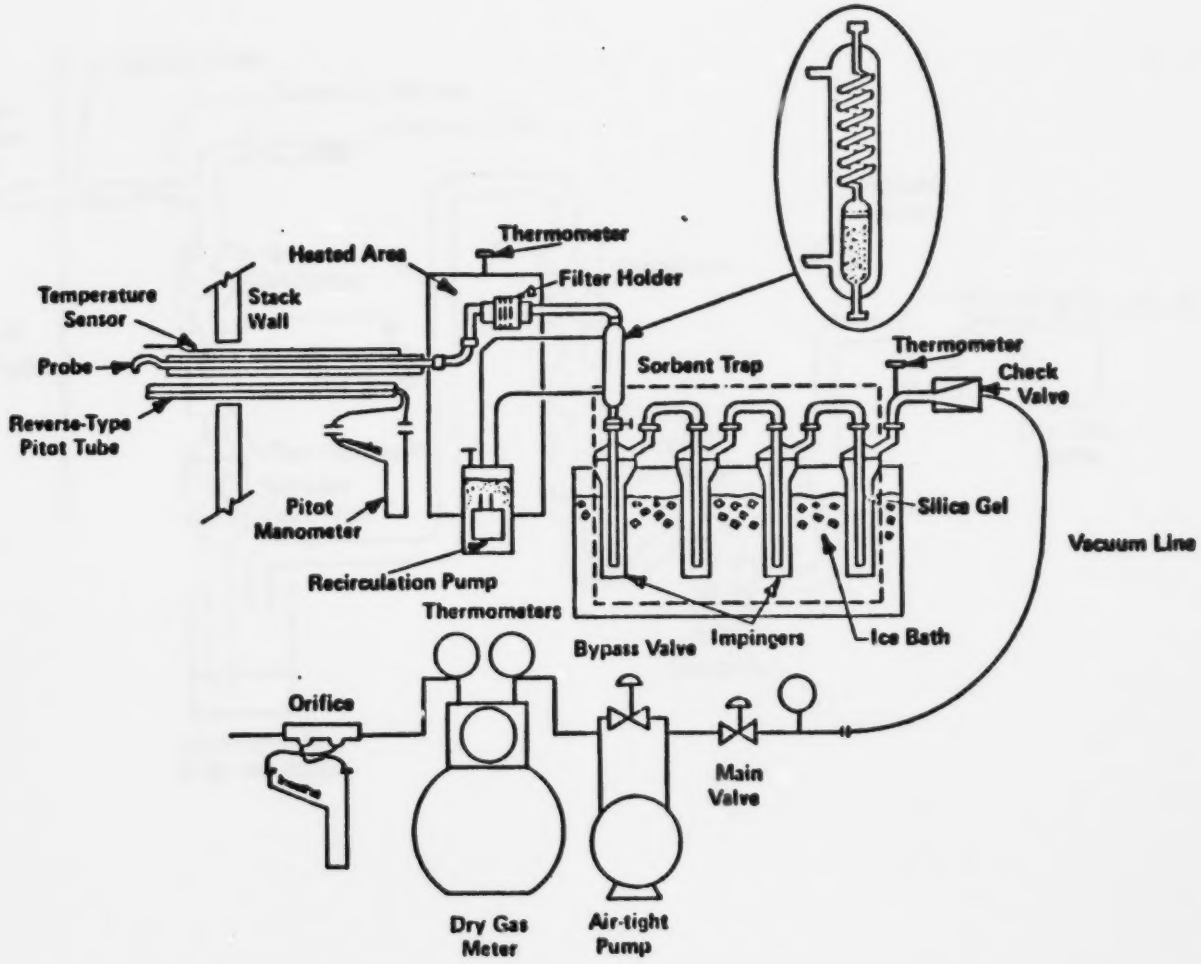


Figure 8-7. Modified Method 5 train.

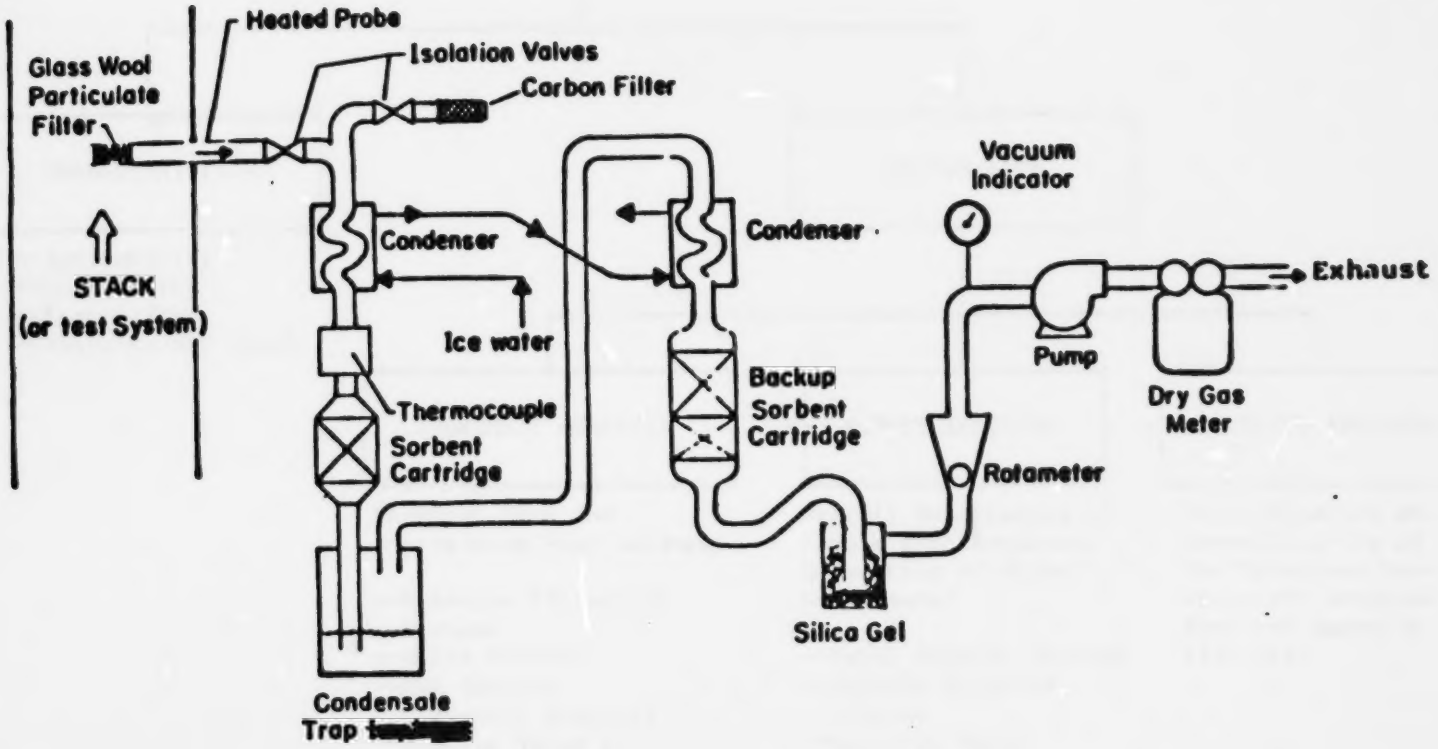


Figure 8-8. Volatile organic sampling train (VOST).

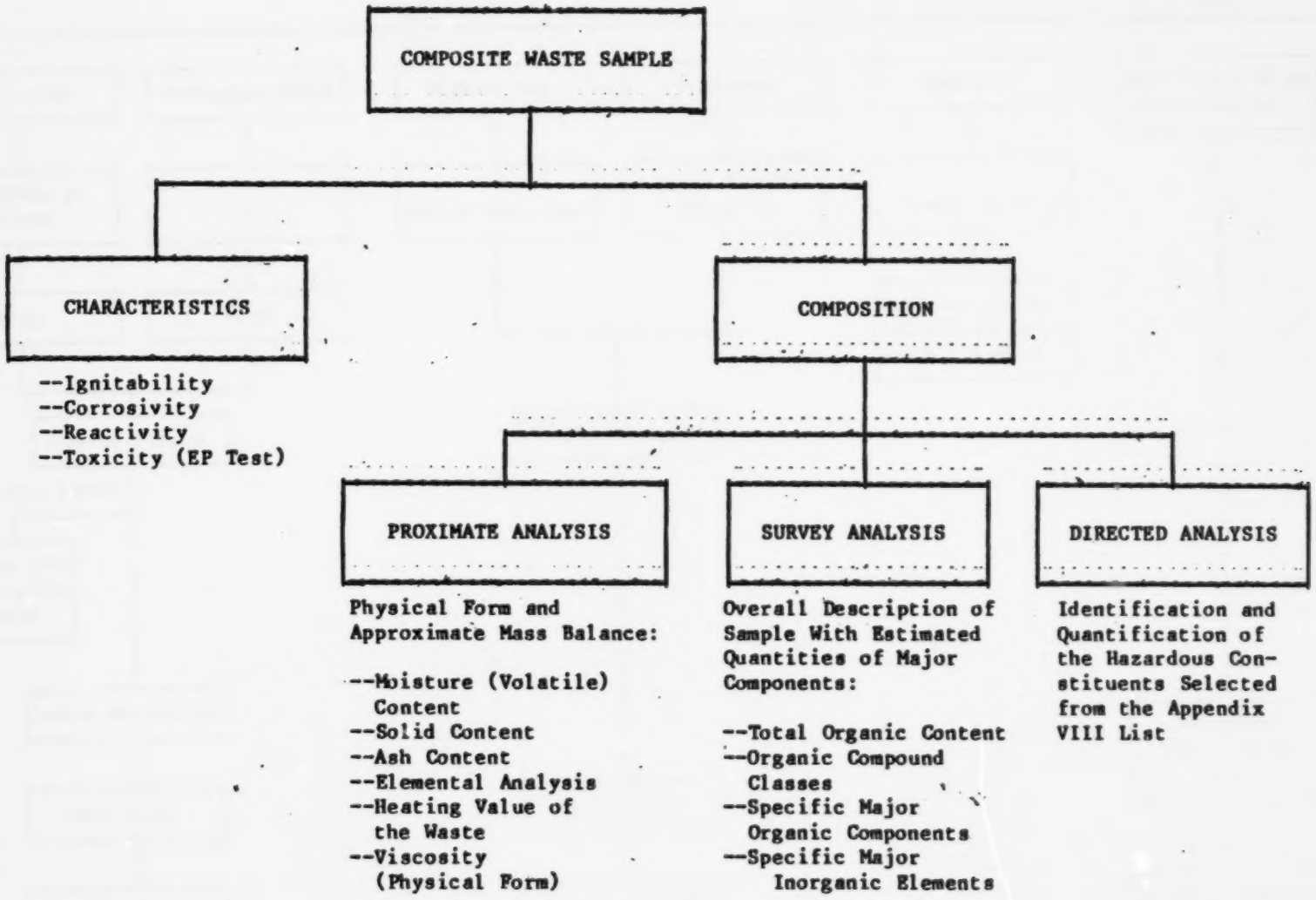
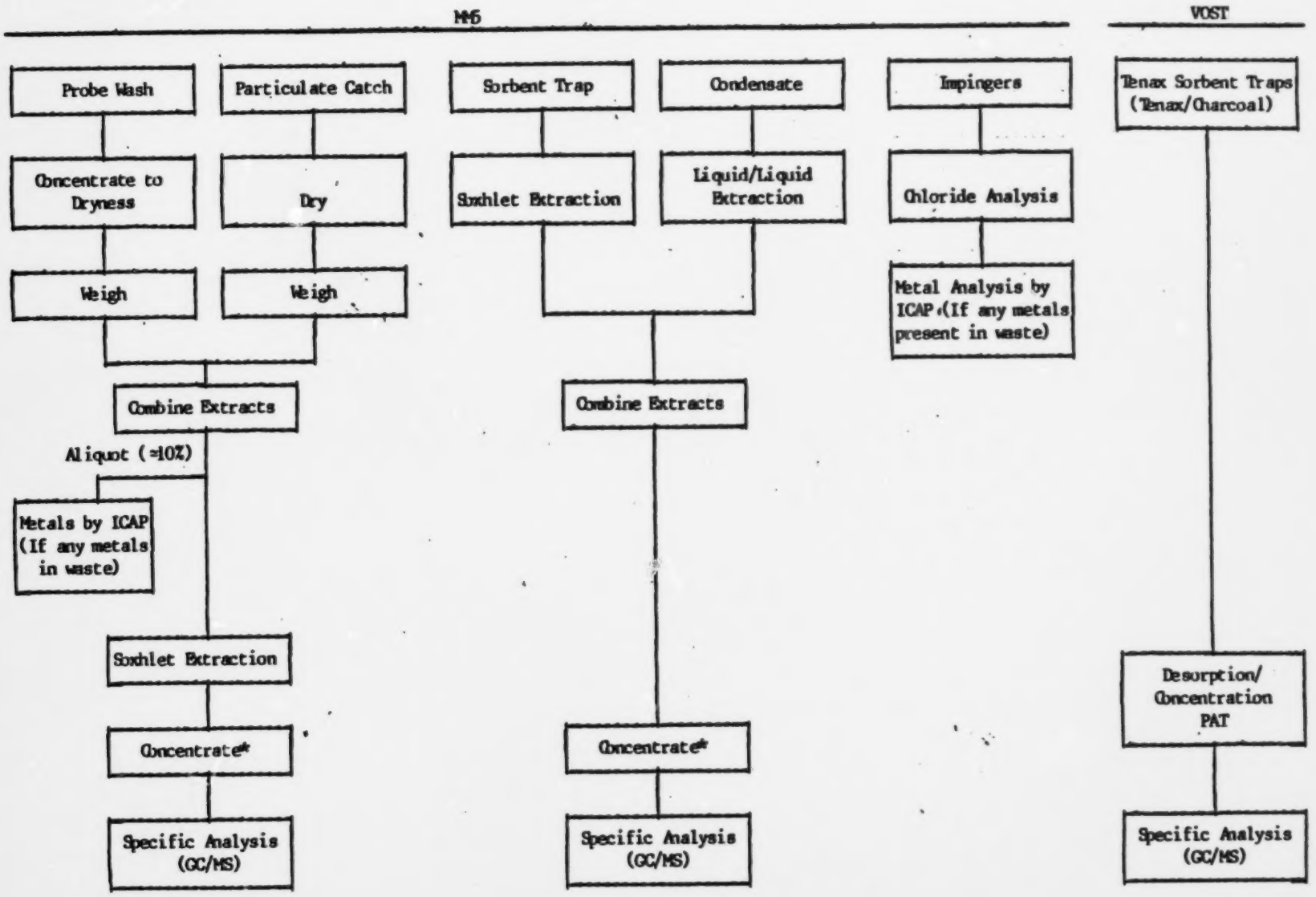


Figure 8-9. Overview of the analytical approach for waste characterization.



*As an alternative, the extracts from particulate and vapor portions of the train may be combined prior to analysis.

Figure 8-10. Overview of analysis scheme for stack gas samples from a comprehensive sampling train.